THE APPLICATION OF ALUMINUM SULPHATE FOR THE IMPROVEMENT OF WATER QUALITY IN LAKES

Ministry
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ALUMINUM SULPHATE

FOR THE IMPROVEMENT OF WATER QUALITY

IN LAKES

by

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ABSTRACT

Aluminum sulphate ($Al_2(SO_4)_3 \cdot 14H_2O$) was used as a nutrient inactivant in an attempt to reverse the eutrophication process in a small southern Ontario farm pond. An enclosure study in eutrophic Moira Lake was conducted to assess the feasibility of a full-scale alum treatment.

In both studies assessments of nutrient and algal removal efficiencies as well as effects on other chemical parameters and treatment permanence were made.

Alum treatment resulted in a 76% and 90% removal of total and dissolved reactive phosphorus in the pond. In addition significant reductions in ammonia and organic nitrogen resulted. Treatment permanence was approximately three months in duration. Dissolved oxygen showed a sharp increase following treatment while pH and alkalinity showed temporary decreases. There was a relatively long-lasting complete reduction in the blue-green *Chroococcus*. Short term improvements in water transparency were seen.

In the Moira Lake nutrient inactivation feability study reduction resulted in total phosphorus (70%), dissolved reactive phosphorus (95%) phytoplankton (76%), ammonia (82%), organic nitrogen (39%), colour (57%) and arsenic (97%). Typical reductions in pH and alkalinity were noted with increases in sulphate and aluminum levels.

Treatment permanence was reduced in the Moira Lake study as a result of discharge water additions simulating actual flow through conditions.

The use of polyethylene enclosures to assess the feasibility of an alum treatment lessened the predictive accuracy of treatment permanence due to containment effects.

Results indicated that treatment of enclosed systems (pond study) is feasible from a cost-benefit point of view while a flow-through system (Moira Lake) presented too many difficulties for consideration of full-scale treatment.

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INTRODUCTION

A large number of lakes in Ontario are in advanced stages of eutrophy due to both natural conditions and man's activities.

The resultant problems of excessive weed growth, nuisance algal blooms, deteriorating fisheries and imparied water quality pose a serious threat to the recreational utilization of these water bodies. The Ontario Ministry of the Environment has been involved in the development of various techniques to curb the eutrophication process.

Approaches to lake restoration fall into two general categories: (1) methods to limit the input of nutrients to the lake (2) within lake procedures to manage the consequences of lake ageing. Limiting nutrient inputs treats the underlying causes of lake problems while procedures for managing the consequences of lake ageing enhance the usability of lakes without controlling the sources of degradation

The most appropriate manner to control eutrophication is to treat the cause rather than the consequences but this cannot always be accomplished. This fact has given rise to the development of "in-lake" remedial measures such as weed harvesting, dredging for nutrient control, artificially induced destratification, hypolimnetic aeration, dilution/flushing, sediment exposure and dessication, lake bottom sealing and nutrient inactivation. This report deals with the use of aluminum sulphate (alum) as a nutrient inactivation and water quality improvement technique.

The process of nutrient inactivation has been defined as "the adding of some type of material that will bond with, adsorb, or otherwise immobilize necessary algal nutrients thus preventing them from being utilized by these organisms for their growth (Environmental Protection Agency, 1973).

In both studies presented here aluminum sulphate was used as a nutrient inactivant to assess the effects of treatment in terms of:

1) nutrient removal capability
2) effects on other chemical parameters such as pH, alkalinity, sulphate and aluminum concentrations.
3) algal removal capabilities
4) permanence of treatment relative to morphometric characteristics and nutrient run-off effects.

LITERATURE SURVEY

Although alum has been used for years as a coagulant for colour and turbidity removal from municipal water supplies and more recently for phosphate removal in domestic waste waters, it was not until 1969 that it was tested for phosphorus removal within a natural body of water.

Jernelov (1970) applied a 50 mg/l dosage of alum to Lake Langsjon in Sweden, a eutrophic, shallow (maximum depth 3m) lake of 35 hectares which received municipal wastes for a number of years. The lake was treated in late April.

The investigators concluded that the aluminum sulphate was effective with respect to total phosphorus reduction as well as reduction in both blue-green and green algal populations. As well, the time between the formation of ice cover and the development of anaerobic conditions was extended. However, the effects of aluminum sulphate were not long-lasting. This may have been due in part to the fact that Lake Langsjon was relatively shallow. Mixing conditions in a shallow, unstratified lake are not as favourable as stratified conditions for alum treatment since the mixing of the bottom waters may interfere with the initial floc settling and, later on, may even resuspend some of the floc.

Shannon and Vachon (1972) studied the feasibility of alum treatment as a water quality control measure on four basins in the third (now abandoned) Welland Canal, Ontario. They used a concentration of approximately 50 mg/l as alum.

The authors concluded that chemical treatment with alum was a feasible method of maintaining acceptable water quality but that nutrient run-off effects were very important in delineating the permanence of the treatment. As in the Lake Langsjon study the factors of shallowness and wind action had a shortening effect on the permanence of the alum treatment. The maximum depth of the Welland Canal treated basin was approximately two meters; similarly, the maximum depth in Lake Langsjon was three meters.

Halsey (Pers. comm.) using polyethylene enclosures measuring 50 square feet in a 12 hectare lake in British Columbia noted that upon application of 50 mg granulated alum per liter of test water orthophosphate and colour levels were significantly reduced with accompanying increases in Secchi disc readings. It should be noted at this point that Halsey applied <u>granulated</u> alum to his

enclosures. Peterson et al. conducted laboratory studies wherein they applied dry (granulated) and slurried alum to containers of lake water. They noted that a poor floc was formed using dry alum and substantial portions of the material settled directly to the bottom of the column. On the other hand slurried alum produced a better floc with greatly improved removals of dissolved and total phosphorus. Had Halsey used slurried alum in his experiment he no doubt would have obtained greater phosphorus and algal removal efficiencies. The entire experiment was repeated the following year (1973). Halsey tentatively stated that "it appeared as if alum could be used as a control agent without the attendant difficulties associated with copper sulphate".

Kennedy and Cooke (1974) injected aluminum sulphate into the hypolimnion of eutrophic Dollar Lake in Ohio. Dollar Lake has an area of 2.2 hectares and a mean depth of 3.9 meters and experiences intense blue-green algal booms, (Cooke and Kennedy 1970). Following treatment there was a substantial reduction in total phosphorus accompanied by increases in water transparency and a drop in net community photosynthesis with a substantial reduction in phytoplankton. The authors are continuing to monitor the lake; however, they felt that it would be surprising if Dollar Lake maintains its clarity and low productivity because of continued inputs from septic drainage and storm waters.

Gahler et al; (unpublished manuscript) treated a one acre farm pond (average depth 2.4 meters) with a neutralized solution of sodium aluminate. A significant improvement in water quality was evidenced by reductions in total phosphate, ammonia, total Kjeldahl nitrogen, iron, manganese and the algal standing crop along with improvements in dissolved oxygen, transparency and pH.

Ree (1963) described the use of alum as an emergency treatment for the control of turbidity in Franklin and Stone Canyon Reservoirs in California. Considerable quantities of material were washed into these reservoirs following heavy rains making them very turbid. The author concluded that although this type of emergency treatment was effective regarding removal of turbidity, it was not intended as a substitute for adequate sanitary protection or from storm water diversion works.

Lin, Evans and Beuscher (1971) studied the removal of algae in natural waters by coagulation with liquid alum in laboratory jar tests. The efficiency of algal removal was found to be dependent upon alum dosage, initial algal concentrations and the types, shapes and other specific characteristics of the

algae. Optimum coagulant dosages for algal reductions was found to be similar to that for turbidity removal.

Bandow (1972) divided a 4,000 square meter fish rearing pond in Minnesota using polyethylene sheeting. The phosphorus content on both sides of the pond was raised to 0.5 mg/1 by adding commercial fertilizer. Slurried alum was applied to one side of the pond at a rate of 1,350 kg/ha. The phosphorus concentration on the experimental side was rapidly reduced by 90%. Aphanizomenon subsequently bloomed on the control side but not on the experimental side. Anabaena bloomed on the experimental side in September (treatment was in May), while Chara and pondweed (Potamogeton spp.) were most dense on the experimental side. Walleye (Stizostedion vitreum) fingerling production was highest on the experimental side. Effects of the treatment on invertebrate production were inconclusive.

A report published by the Office of Air and Water Programs, Division of Water Quality and Non-Point Source Control and the Office of Research and Development; National Eutrophication Research Program (1973) on the subject of nutrient inactivation stated that many problems remained to be answered before this technique can be considered operational. These problems were:

1) The relatively high expense of treating a large body of water.

2) Possible toxic effects on the biota by or through the introduction of an excess of aluminum.

3) Adverse biological effects from the formation of a floc. The material used may be non-toxic but the floc could conceivably suffocate aquatic organisms by interfering with their respiratory mechanisms. It is also possible that the floc material resting on the sediments could interfere with the benthic ecology of the system.

4) To obtain maximum effectiveness, it may be necessary to either raise or lower the pH of the system which could have serious biological consequences.

5) The addition of certain salts, such as sulphates and chlorides may increase the conductivity of the water to an unacceptable level. In the case of sulphate, if the hypolimnetic waters should become anaerobic after treatment, reduction of the sulphate would lead to the release of hydrogen sulphide.

6) The time of application of the inactivant may be critical. It may be necessary to apply the material when the maximum nutrient content is present in the water.

7) Little information is available on the effective duration of the treatment. Wind action, continued inflow of nutrients and bacteriological and benthic organism activity are a few of the phenomena which could possibly influence the longevity of treatment effects.

Based on the literature, it is apparent that nutrient inactivation using aluminum sulphate is a viable lake restoration technique. However, there are limitations to this technique. Lake morphometry, size of drainage basin, effects on biota, run-off effects, lake retention time and economic restrictions from a cost-benefit point of view are parameters which should be thoroughly delineated in any nutrient inactivation study.

M.T.R.C.A. POND

Site Description

The M.T.R.C.A. Pond is located in Peel County, Albion Township approximately 1.5 miles north of the town of Bolton on the west side of Highway 50 on a farm owned by the Metropolitan Toronto and Region Conservation Authority. The pond lies in a small hollow and is very well sheltered. The pond has a surface area of 638 m^2 with an average depth of 1.1m and a volume of 680 m^3. Maximum depth is 2.7 meters (Figure 1).

Construction of Polyethylene Barrier

A 6 mil thick black polyethylene curtain was placed to bisect the pond lengthwise for the purpose of affecting control and treated portions.

Sampling Techniques

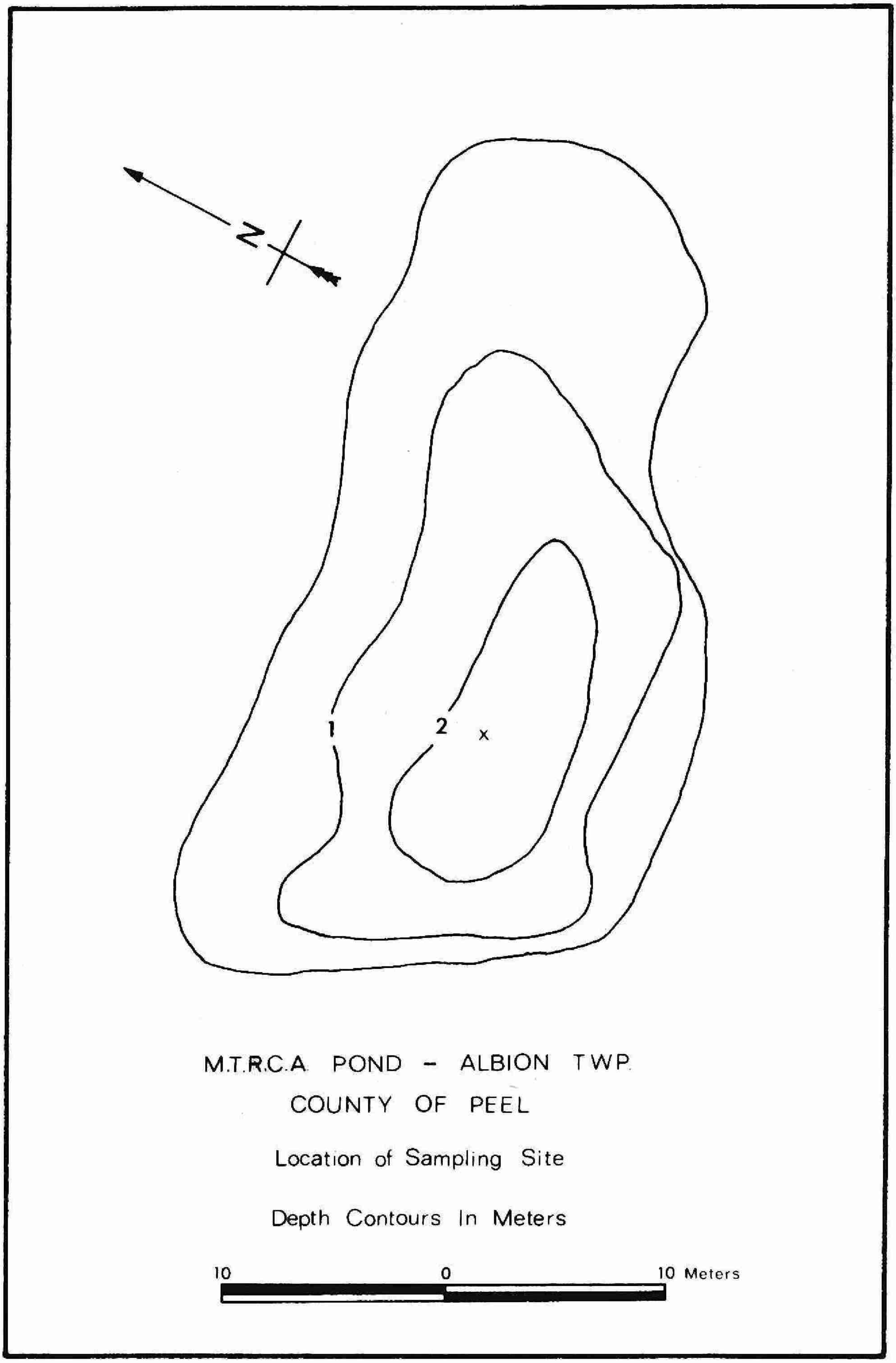
From the initiation of sampling on July 20, 1973 to October, 1973 samples were taken with a 6 liter Van Dorn bottle at 0.5m intervals from the surface of the pond to 2.0m. From November 2, 1973 to the termination of the study on November 7, 1974 samples were taken using a custom made sampling device comprised of a small brass bilge pump coupled to a graduated length of hose with a small weighted water intake. In order to obtain a representative composite sample from the pond's surface to a depth of 2.0m the volume of water taken from each stratum was proportional to the volume of that stratum. Water samples were taken at depths of 0.25, 0.75, 1.25 and 1.75m representing 0.5m thicknesses. Bottom water samples were taken at a depth of 2.5m and were treated separately.

In order to correlate the data collected from July 20 to October 17, 1973 with the data collected in the predescribed manner, results of analyses for different strata were weighted according to the volumes of the strata. In this manner data from both sampling periods were comparable.

Analytical Techniques

Water temperatures were recorded at 1.0m intervals in the water column by immersing a standard pocket thermometer into the sample container at the

FIGURE 1: M.T.R.C.A. POND CONTOUR MAP



time of sampling. Dissolved oxygen profile measurements were made using the Winkler method. Additions of manganese sulphate and alkalide azide were made in the field. Addition of the sulphuric acid reagent and titrations with sodium thiosulphate were carried out in the laboratory.

Chlorophyll a samples were preserved in the field with 1 ml of a 2% suspension of magnesium carbonate. Algal samples were preserved with sufficient Lugol's solution to impart a dark orange colour to the water.

Chlorophyll, algal and chemical samples were transported to the Ministry of the Environment's Division of Laboratories in Toronto for analysis. All sample preservation techniques and analyses were done in accordance with Outline of Analytical Methods, Ontario Ministry of the Environment (1974).

Jar Test Procedures

In order to ascertain the appropriate aluminum sulphate concentration for removal of a significant portion of the nutrients surface water samples were obtained from the pond one week prior to the proposed treatment date. Duplicate tests were run at concentrations of 100, 150, 200 and 250 mg alum/l. added in slurry form. The contents were stirred for two minutes and the floc was allowed to settle for three hours. Samples were siphoned off and submitted to the Laboratories Branch for analysis of pertinent parameters.

Alum Application

Based on an alum dose of 250 mg/l. a volume of 3.84×10^5 liters (volume of treated pond section) was treated with 211 pounds of aluminum sulphate ($Al_2(SO_4)_3 \cdot 14H_2O$). Dry alum was mixed with pond water in a large plastic vat until a slurry had formed. This slurry was applied to the treated portion of the pond by "bucketing" the slurried alum into the propwash of a 4 h.p. outboard mounted on a small pram to insure maximum contact of the slurry with the pond water. The pram was run in transects parallel to the shoreline to insure uniform distribution of the alum slurry.

Upon application of the alum slurry the pond water turned a "milky" colour but no large floc particles materialized. It was hypothesized that due to over-mixing the floc particles were not allowed to form to their maximum size and hence would explain why it required almost one week for this floc to precipitate to the pond bottom.

THEORETICAL REACTIONS OF ALUMINUM SULPHATE

Lea, Rohlich and Katz (1954) defined the hydrolysis of aluminum sulphate by the formula:

1) $Al_2(SO_4)_3 \cdot 14H_2O + H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4$

Based on this reaction 594 gms of $Al_2(SO_3)_3 \cdot 14H_2O$ will produce 294 gms of H_2SO_4. The sulphuric acid then reacts with calcium bicarbonate ($Ca(HCO_3)_2$).

2) $3Ca(HCO_3)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 6H_2O + 6CO_2$

The reaction of 294 gms. of H_2SO_4 with $Ca(HCO_3)_2$ yields 408 gms. of $CaSO_4$ and 264 gms of CO_2.

With equations (1) and (2) and with a known aluminum sulphate concentration calculations can be made that will predict the concentrations of CO_2, $CaSO_4$ (loss in alkalinity), and SO_4 that will result from an alum treatment. These hypothetical results can then be compared with the actual measurements to ascertain a degree of efficiency. The following equations describe the predicted changes in the various parameters based on the aforementioned hypothetical reactions.

1) Aluminum

Theoretical [Al] increase $[Al_{Th}]$

$$[Al_{Th}] = \frac{a \cdot b}{c}$$

a = mol. wt. of Al

b = alum concentration used (mg $Al_2(SO_4)_3 \cdot 14H_2O/l$)

c = mol. wt. of $Al_2(SO_4)_3 \cdot 14\ H_2O$

Observed [Al] increase $[Al_{OB}]$

Al_T = [Al] following treatment

$$[Al_{OB}] = [Al_T] - [Al_{BG}]$$

Al_{BG} = background [Al]

By subtracting the observed aluminum increase from the theoretical increase an estimate can be made as to the amount of aluminum that presumably participated in floc formation and subsequently precipitated out of solution.

$$\%\ Efficiency = 100 - \frac{[Al_{OBS}]}{[Al_{Th}]} \times 100$$

2) Alkalinity

Theoretical decrease in alkalinity $[Alk_{Th}]$

$[Alk_{Th}]$ = $^{b}/_{1.46}$

$$1.46 = \frac{\text{mol. wt. of } Al_2(SO_4)_2 \cdot 14H_2O}{\text{mol. wt. } 3CaSO_4}$$

b = alum concentration used ($mg\ Al_2(SO_4)_3 \cdot 14H_2O/l$)

Observed alkalinity reduction

$[Alk_{OBS}] = [Alk_{BG}] - [Alk_T]$

Alk_T = alkalinity after treatment

Alk_{BG} = background alkalinity (before treatment)

$$\% \text{ Efficiency} = \frac{[Alk_{OBS}]}{[Alk_{Th}]} \times 100$$

In discussing theoretical reactions of aluminum sulphate Cohen and Hannah (1971) stated that "1 mg/l of alum reacts with 0.50 mg/l natural alkalinity expressed as $CaCO_3$." It can be seen that the formula for alkalinity reduction $[Alk_{Th}]$ given above correlates well.

3) Sulphate

Theoretical SO_4 increase $[SO_{4Th}]$

$$SO_{4Th} = \frac{d \cdot b}{c}$$

d = mol. wt. of $(SO_4)_3$

b = alum concentration used. ($mg\ Al_2(SO_4)_3\ 14H_2O/l$)

c = mol. wt. of $Al_2(SO_4)_3\ 14H_2O$

Observed SO_4 increase

$[SO_{4OBS}] = [SO_{4T}] - [SO_{4BG}]$

SO_4 = SO_4 concentration after treatment.

SO_{4BG} = background SO_4 (before treatment)

$$\% \text{ Efficiency} = \frac{[SO_{4Th}]}{[SO_{4OBS}]} \times 100$$

RESULTS AND DISCUSSION

Jar Tests

Phosphorus

Alum concentrations of 100, 150, 200 and 250 mg/l reduced total phosphorus concentrations to 25, 23, 18 and 16 μg P/l respectively from a control value of 120 μg P/l (Figure 2). These residual total phosphorus values corresponded to 79, 81, 85 and 87% removals.

With an alum concentration of 100 mg/l dissolved reactive phosphorus was reduced from 88 to 2 μg P/l (detection limit). This corresponded to a 98% removal.

pH

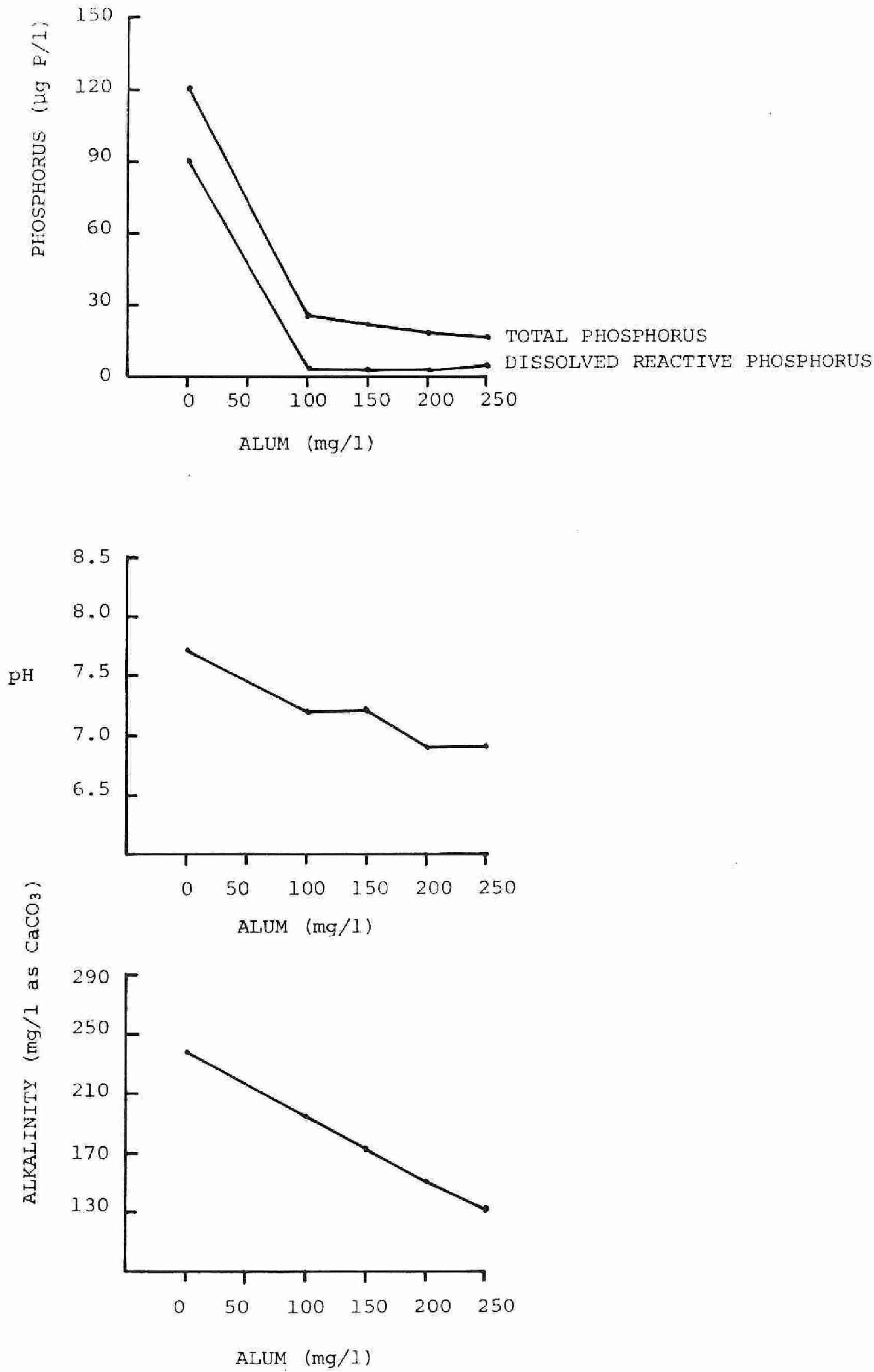
A 250 mg/l alum dose resulted in a decrease of 0.8 pH units from a control value of 7.7 down to 6.9 (Figure 2b). Generally speaking there was a progressive drop in pH with an increase in alum concentration.

Alkalinity

Alkalinity values demonstrated an inverse linear relationship with increases in alum concentration. With an application of 250 mg alum/l maximum reduction in alkalinity was observed (from a control value of 238 to 130 mg/l as $CaCO_3$)(Figure 2c.) With a theoretical alkalinity reduction of 178 mg/l as $CaCO_3$ and an observed alkalinity reduction of 108 mg/l as $CaCO_3$ this corresponded to a treatment efficiency of 61%.

Although the jar tests indicated that a 100 mg/l alum dose was sufficient to remove 79% of total phosphorus and 98% of the dissolved reactive phosphorus without producing extreme decreases in alkalinity and pH it was decided to use an alum concentration of 250 mg/l based on a subjective determination of maximum water clarity.

FIGURE 2: REDUCTIONS IN PHOSPHORUS, pH AND ALKALINITY IN JAR TEST ALUM TREATMENTS



Field Studies

On August 28, 211 lbs of aluminum sulphate was applied in slurry form to the south half of the pond. Chemical data later indicated that the polyethylene barrier was ineffectual in maintaining a viable control portion.

Increases in sulphate and decreases in alkalinity concentrations indicated that the barrier was leaking, however, these sulphate and alkalinity changes were not as severe as those seen in the treated portion. This indicated that the control portion was exposed to a slow leak of hydrolyzed aluminum sulphate. pH values in the control portion showed no decrease as a result of this leak whereas the treated portion showed a sharp decrease following alum treatment. All data presented herein are for the treated portion of the pond with some control portion data for comparison.

Water Transparency

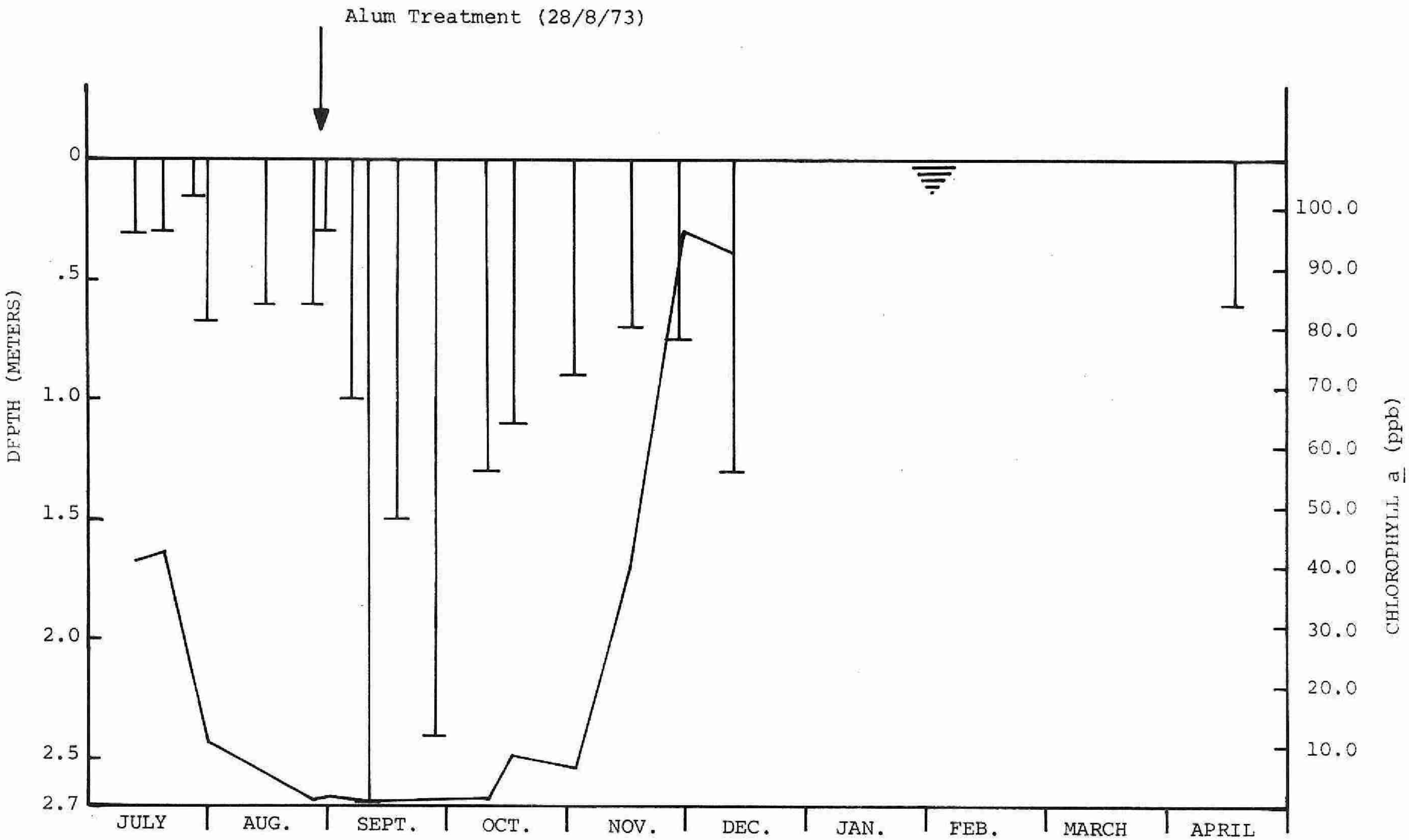
Secchi disc values prior to treatment ranged from 0.15 to 0.70m (Figure 3). On August 28 (treatment date) a pre-treatment Secchi disc value of 0.6m was evidenced. Two days following treatment the Secchi disc value was only 0.3m. This reduced value was due to the "milky" colour of the water imparted by poor floc formation. Maximum water transparency was obtained on September 11 when the Secchi disc was viewed sitting on the bottom of the pond on both the control and treated portions (2.7m). Throughout October and November Secchi disc readings gradually became reduced until November 16 when a Secchi disc reading of 0.7m indicated that water transparency had returned to pre-treatment levels.

Chlorophyll *a*

Due to low chlorophyll *a* concentrations at the time of treatment no demonstrable results were seen. Following alum treatment, chlorophyll *a* values remained below 2.0 ppb. until October 17 after which the photosynthetic pigment started to show an upward trend. Chlorophyll *a* levels in the control portion tended to be slightly higher than those in the treated portion throughout the study period. During the month of November, chlorophyll *a* values in the treated portion showed a sharp increase to a maximum value of 96 ppb. on November 30. It is difficult to assess whether this demonstrates a seasonal trend due to a lack of a viable control.

As demonstrated in Figure 3 a reduction in chlorophyll *a* values corresponded to an increase in Secchi disc readings prior to treatment.

FIGURE 3: SECCHI DISC READINGS AND CHLOROPHYLL a VALUES BEFORE AND AFTER ALUM TREATMENT



However, under the influence of an alum treatment while chlorophyll a values were very low there was a marked improvement in water transparency. Although colour and turbidity measurements were not taken it appeared as if the increase in water transparency was due to a removal of colour and/or turbidity by the alum treatment. Post-treatment reductions in water transparency were in all probability due to a combination of increases in phytoplankton standing crop, turbidity increases due to run-off effects and the effect of winds on the shallow pond.

Phytoplankton Standing Stocks

Table 1 shows the composition of surface algal samples taken before and after alum treatment. During the pre-treatment period the phytoplankton standing crop was dominated by the flagellates Rhodomonas minuta and Cryptomonas curvata. The blue-green algae were represented only by Chroococcus. Following alum treatment there was a virtual irradication of the blue-green Chroococcus. Slight reduction in the flagellates was seen following treatment but these numbers increased dramatically in the ensuing months. Slight reductions in green algae (specifically Schroederia) and increases in the diatom Nitzschia were seen following treatment. September and October increases in diatoms was probably due to the almost complete removal of Chroococcus coupled with slight reductions in the flagellates and green algae.

Any further observations regarding the effect of alum treatment on the population dynamics of algal species would be speculative in nature due to the lack of a good control for comparison.

Macrophytes

Prior to treatment, sparse growth of Potomogeton strictifolius was witnessed only in the shallow east end of the pond. Due to increased water transparency induced by the alum application increases in the density and ranges of pondweed were observed. There was much higher growth in the shallow portions of the pond and this growth was observed to a greater depth than seen before treatment. These observations concur with those of Kennedy and Cooke (1974) who observed that

Table 1: M.T.R.C.A. Pond Phytoplankton Standing Stocks (a.s.u./ml).

Date	Blue-Greens	Flagellates	Greens	Diatoms	Total
July 20	72	2797	49	17	2935
Aug. 1	39	1282	80	0	1401
Aug. 15	39	379	36	0	454
Aug. 27	90	579	284	0	953
Aug. 30	123	589	108	0	820
Sept. 11	2	436	119	25	582
Sept. 18	0	210	107	22	339
Oct. 17	0	1155	0	5	1160
Nov. 29	15	3253	14	18	3300
Jan. 15	0	29136	3	0	29139

Note: Alum treatment on August 28th.

following alum application to eutrophic Dollar Lake, photosynthetic activity of *Oscillatoria* mats on the sediment increased.

Total Phosphorus

Immediately following treatment there was a 76% removal of total phosphorus from 140 µg P/l (August 27) to 34 µg P/l on September 28. (Figure 4). From the minimum level, total phosphorus gradually increased to pre-treatment concentrations by December 9. Increases in total phosphorus content after September 27 can be attributed to a combination of heavy nutrient runoff due to autumn rains as well as probable resuspension of nutrients due to the effect of winds on the relatively shallow pond. Other investigators have remarked on these factors as being responsible for nutrient increases (Shannon and Vachon, 1972; Kennedy and Cooke, 1974; Graham and Hunsinger, 1972).

These nutrient inputs are reflected in increases in phytoplankton standing stocks, a gradual lessening of water transparency as well as increases in chlorophyll *a* levels.

Dissolved Reactive Phosphorus

Dissolved reactive phosphorus concentrations showed a dramatic drop from 60 µg P/l to 6 µg P/l (90% removal) immediately after treatment (Figure 5). Dissolved reactive phosphorus levels remained below 9 µg/l until early December after which gradual increases were noted until pre-treatment levels were evidenced in late March. A comparison of dissolved reactive phosphorus results along with total phosphorus (Figure 4) and phytoplankton standing stock data (Table 1) indicated that there were two possible sources of nutrients to explain increases in chlorophyll *a* content, total phosphorus and algal populations with attendant low dissolved reactive phosphorus levels. Firstly, nutrients introduced by runoff effects may have been quickly assimilated by suspended algae. Secondly, mixing of the sediment by wind action and the subsequent assimilation of the resuspended nutrients by algae would result in increases in chlorophyll, total phosphorus and phytoplankton standing stocks. This would explain why dissolved reactive phosphorus levels were low for such a long duration. Any forms of available phosphorus would be incorporated into the algal population thus resulting in increased levels of chlorophyll *a*, phytoplankton and total phosphorus without increasing dissolved reactive phosphorus levels to any appreciable extent.

FIGURE 4: TOTAL PHOSPHORUS BEFORE AND AFTER ALUM TREATMENT

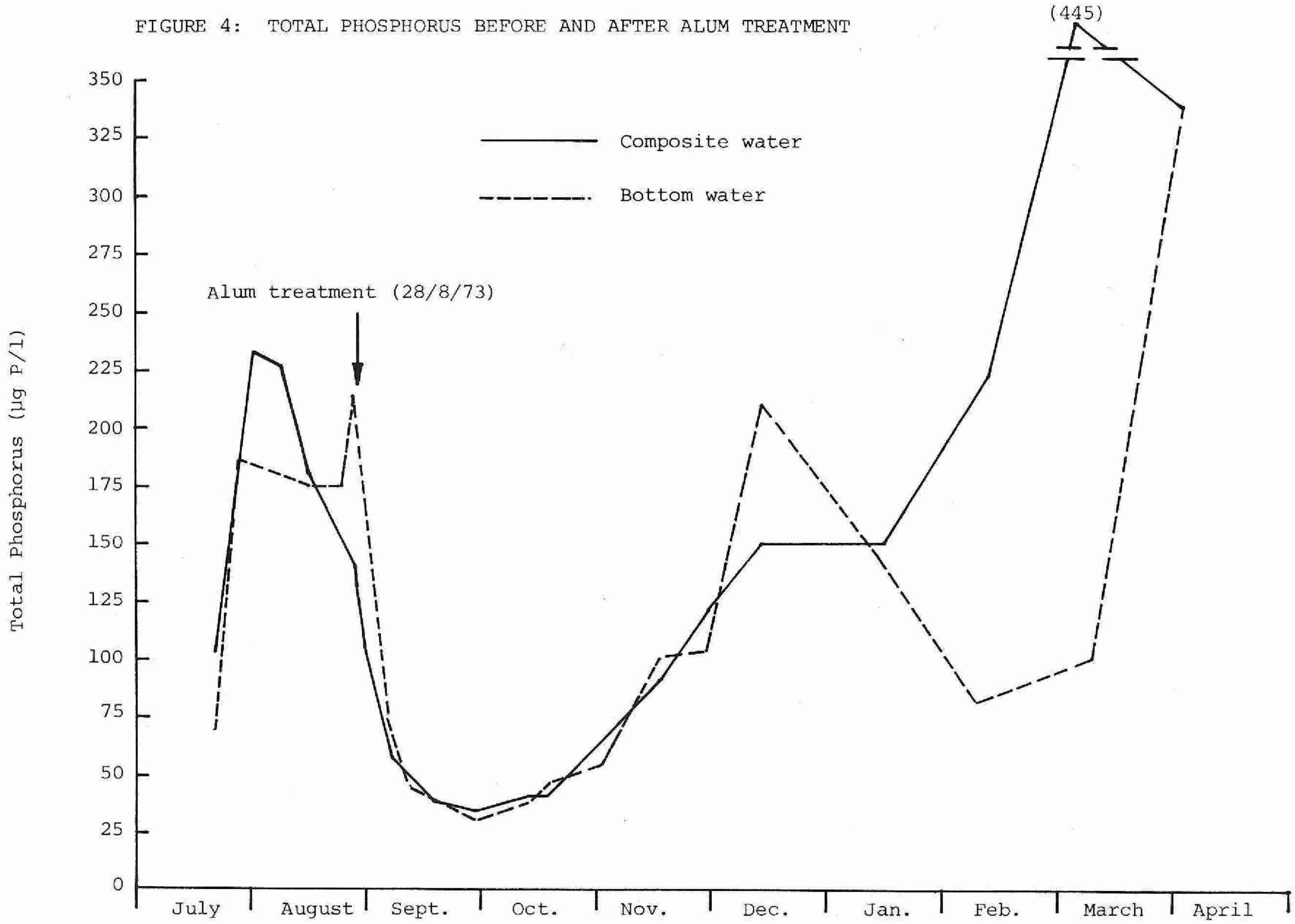


FIGURE 5: DISSOLVED REACTIVE PHOSPHORUS BEFORE AND AFTER ALUM TREATMENT

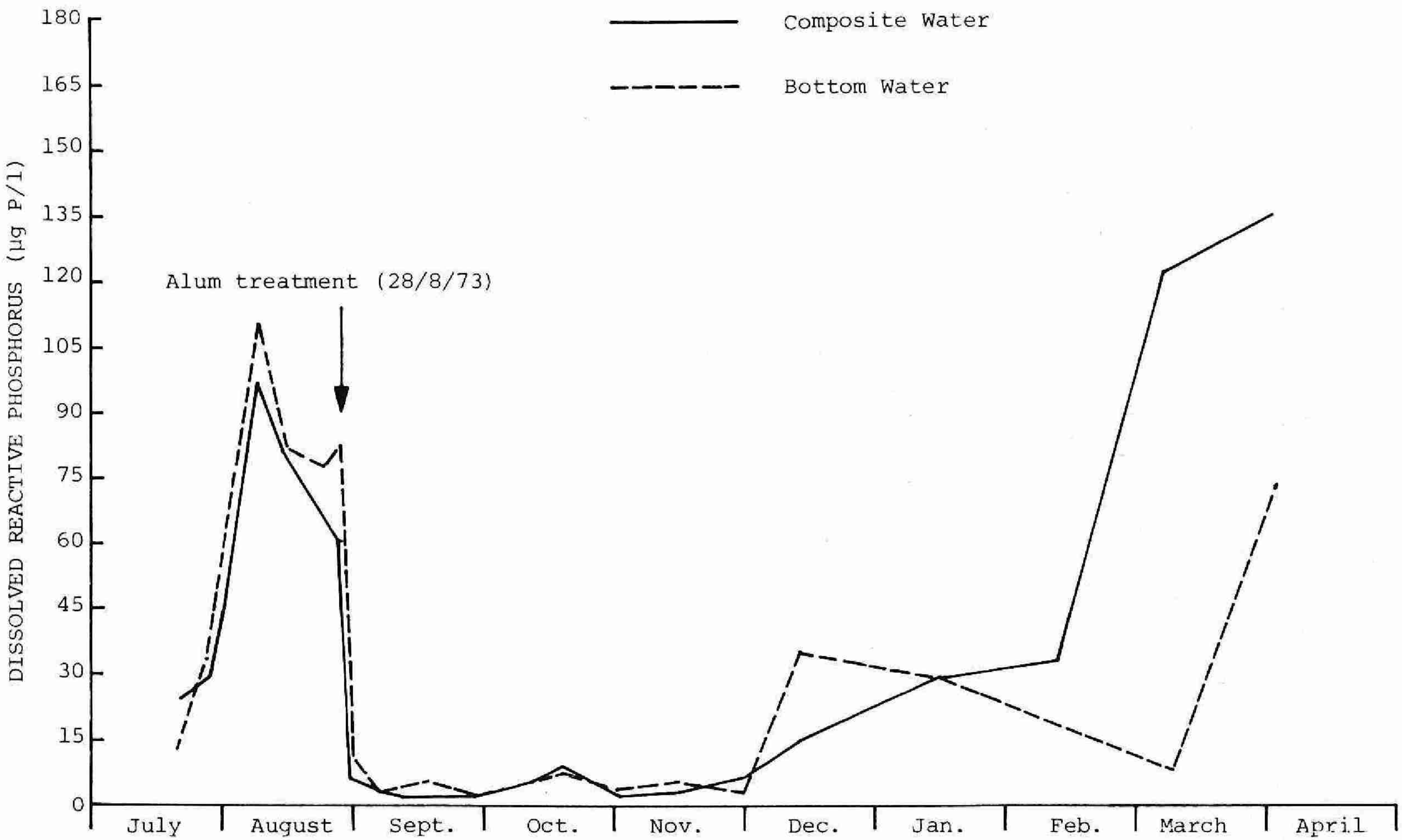
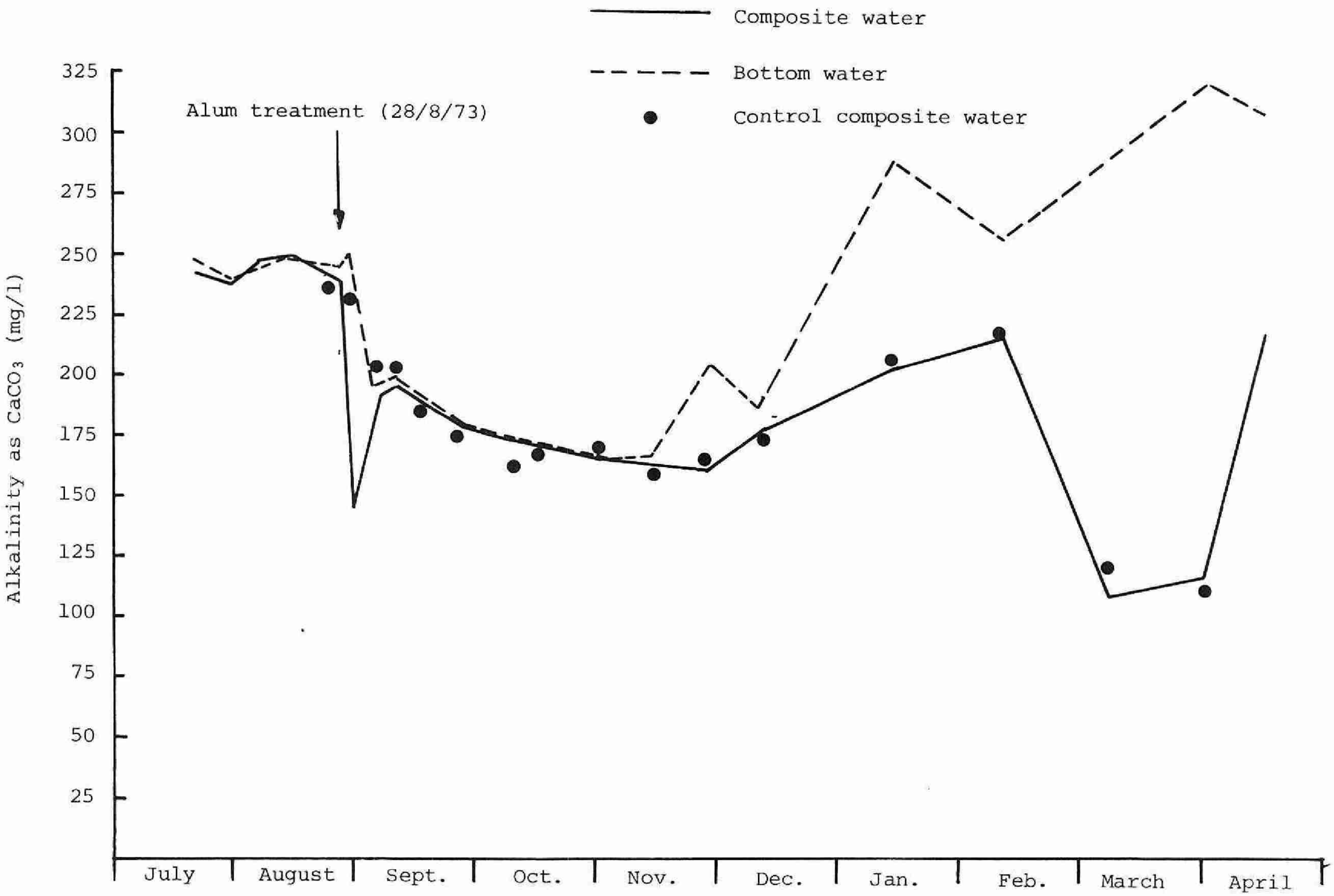


FIGURE 6: ALKALINITY BEFORE AND AFTER ALUM TREATMENT.



Alkalinity

Alkalinity values prior to treatment were 240 mg/l as $CaCO_3$ (composite) and 245 mg/l as $CaCO_3$ for the bottom water (Figure 6). Following alum treatment composite alkalinity dropped from 240 mg/l as $CaCO_3$ to 143 mg/l as $CaCO_3$. This corresponds to an observed reduction of 97 mg/l as $CaCO_3$. Based on a 250 mg/l alum dose alkalinity reduction of 171 mg/l as $CaCO_3$ would be expected. This yielded only a 57% efficiency in alkalinity reduction in the treated portion. Assuming, however, that approximately 50% of the alum leached into the control portion, alkalinity reduction of 86 mg/l as $CaCO_3$ is obtained. When this is compared to the observed reduction of 97 mg/l as $CaCO_3$ an 89% efficiency is obtained.

This correlates rather well with the observed reduction in alkalinity in the control portion (235 to 163 mg/l as $CaCO_3$) and yields an efficiency of 74%.

These calculations seem to indicate that the entire pond was subjected to an alum dose of 125 mg/l rather than 250 mg/l (treated portion) and substantiates the observation that control parameters underwent the same fluctuations as did the treated portion parameters following treatment.

Alkalinity in the bottom waters (treated portion) demonstrated a slight lag in reduction, probably due to the time element involved in floc precipitation. Also, the drop in alkalinity was not of the same magnitude as seen in the composite results (245 mg/l to 195 mg/l as $CaCO_3$). Following the initial drop in composite water alkalinity there was a sharp increase to a value of 190 mg/l as $CaCO_3$. Following this, both composite and bottom water alkalinities remained uniform for a period of a little more than two months. From mid-November through to mid April there was definite divergence of alkalinity values in composite and bottom waters. Alkalinities sharply increased in the bottom water while alkalinity values showed a slight increase and then a sharp decrease in the composite waters.

During the months of November through February, large increases in phytoplankton standing stocks (specifically flagellates) were evident in the surface waters while bottom water samples showed no appreciable increase in flagellate populations. This phenomenon is reflected in alkalinity values.

In the upper strata of the pond during photosynthesis the flagellates were assimilating free carbon dioxide in large quantities. These losses in free CO_2 could only be compensated by the conversion of bicarbonate to carbonic acid and free CO_2. This had the effect of repressing increases in the alkalinity content of the water.

A combination of low phytoplankton standing stocks and high CO_2 levels (on January 15 bottom water CO_2 was 33.0 ppm) in the bottom waters indicated that not only would there probably be no loss of bicarbonate but that the excess of CO_2 would drive the equilibrium toward the production of bicarbonate and hence raise alkalinity values. This in fact is what was observed.

pH

Pre-treatment pH values for composite and bottom water were 8.0 and 7.3 respectively. Upon addition of aluminum sulphate and resultant production of aluminum hydroxide and hydrogenous pH values in the water column dropped 1 pH unit (Figure 7). pH dropped 0.7 pH units in the bottom water. There was a recovery of pre-treatment pH levels by September 15th. From November 9th to the duration of the study, pH levels in the bottom waters was always less than that of composite values. Relatively higher pH values in composite waters reflected higher productivity levels in these waters as compared to bottom water as reflected in chlorophyll a concentrations.

Organic Nitrogen

Some variability was seen in pre-treatment composite organic nitrogen values (range 0.45 to 1.65 mg N/l); however, quick reductions in both composite and bottom water samples on August 30th could be attributed in part to the loss of a portion of the algal population as a result of alum treatment (Figure 8). Bottom water organic nitrogen underwent a 50% (1.80 to 0.90 mg N/l) removal while composite values demonstrated a 20% removal (1.49 to 1.19 mg N/l). It is unlikely that observed algal reductions (953 to 820 a.s.u./ml in composite water and 302 to 263 a.s.u./ml in bottom water) are first of all significant changes and secondly that these changes would account for the aforementioned losses in organic nitrogen. The existence of organic compounds present in either true or colloidial solution other than that incorporated into the phytoplankton and the subsequent removal by alum treatment would explain the organic nitrogen loss over and above algal removal. Under ice-cover in mid-January lower levels in organic nitrogen in bottom waters relative to levels in composite waters reflects the presence of a large population of *Cryptomonas curvata*.

Ammonia Nitrogen

Composite and bottom water ammonia levels dropped sharply following treatment. On September 11th ammonia levels in composite and bottom waters were both

FIGURE 7: pH BEFORE AND AFTER ALUM TREATMENT

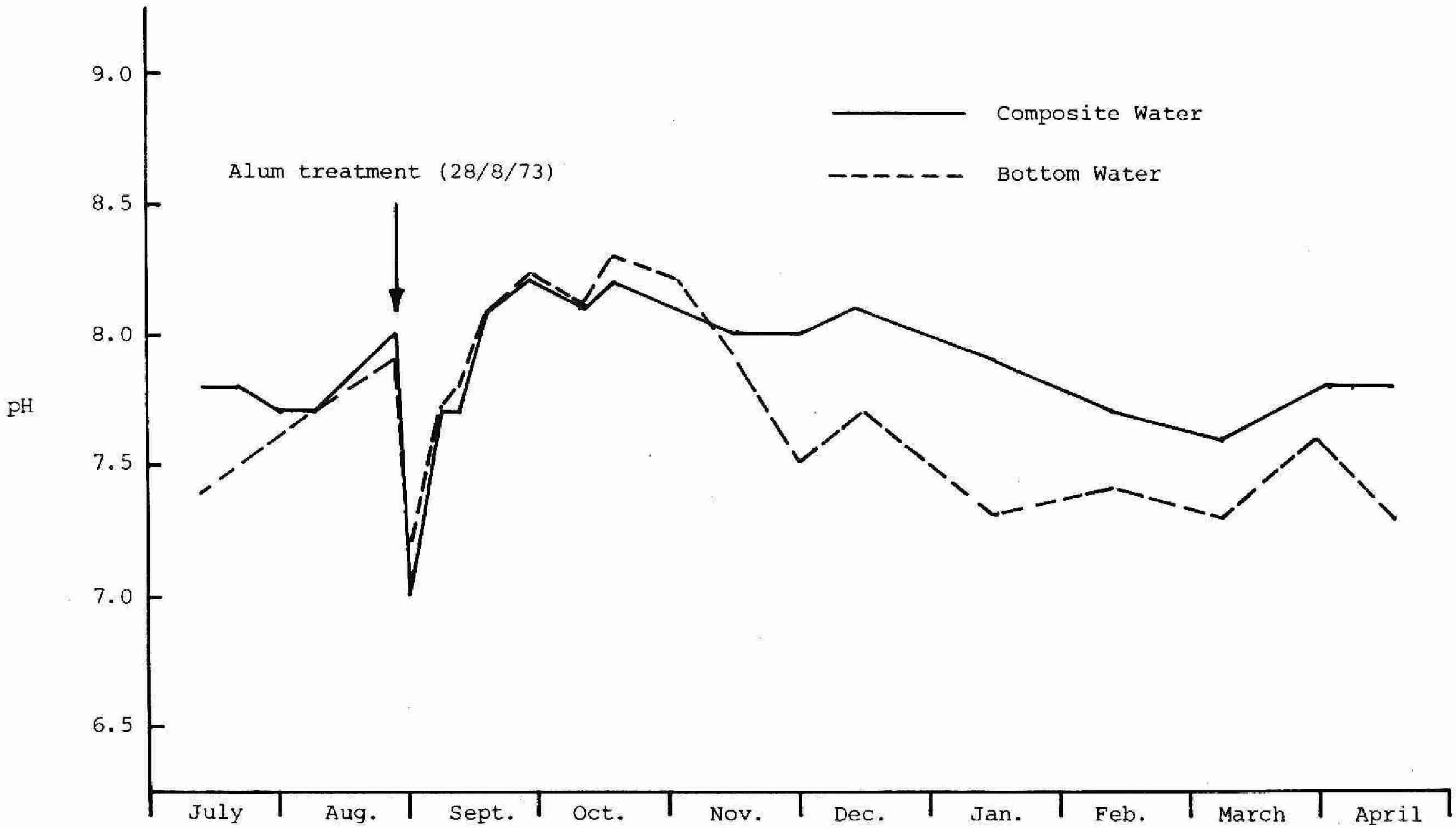


FIGURE 8: ORGANIC NITROGEN VALUES BEFORE AND AFTER ALUM TREATMENT.

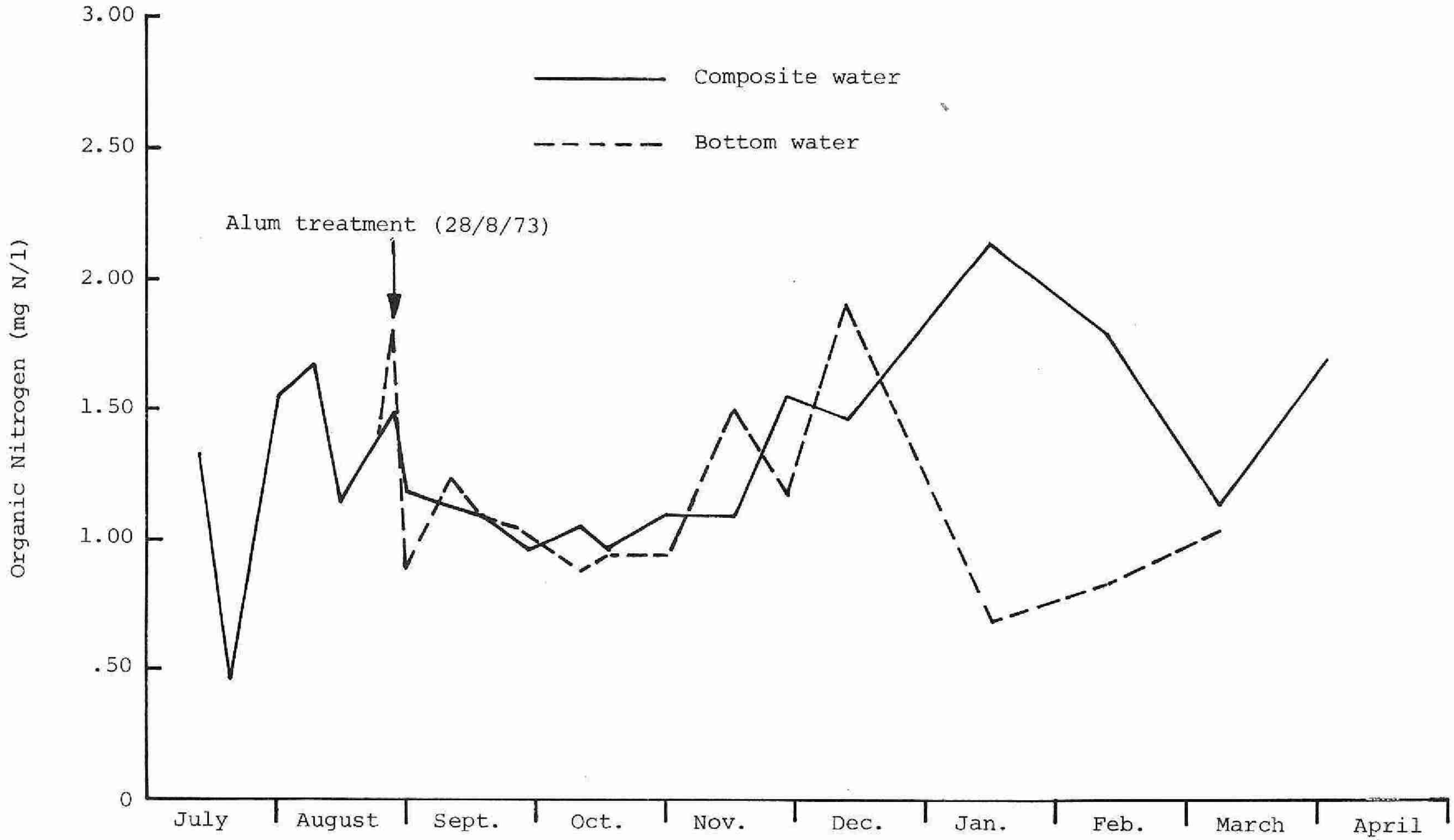
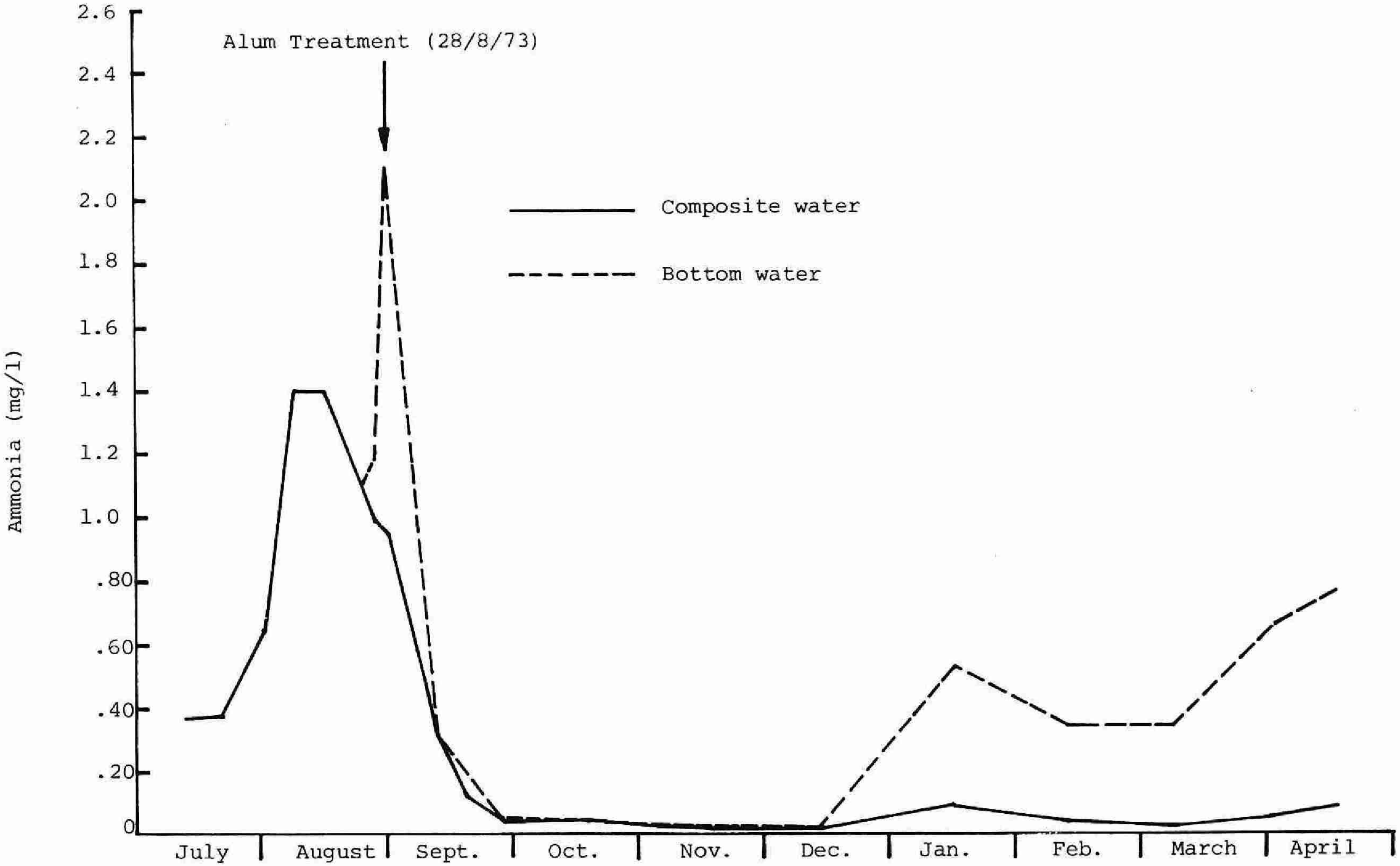


FIGURE 9: AMMONIA BEFORE AND AFTER ALUM TREATMENT



0.32 mg N/l as compared to pre-treamtent levels of 0.99 and 2.1 mg/l respectively. From September 28th through to mid-December levels never exceeded 0.06 mg N/l. The fact that there were such large reductions in not only ammonia but nitrite and nitrate nitrogen suggests that alum treatment may have inhibited the decomposition of organic material by precipitating out a large portion of the bacteria responsible for the nitrification process. Increases in bottom water ammonia levels with attendant increases in nitrite and nitrate nitrogen from mid-December through to April suggests that the decomposition process was once again functioning and had overcome the effects of treatment.

Dissolved Oxygen

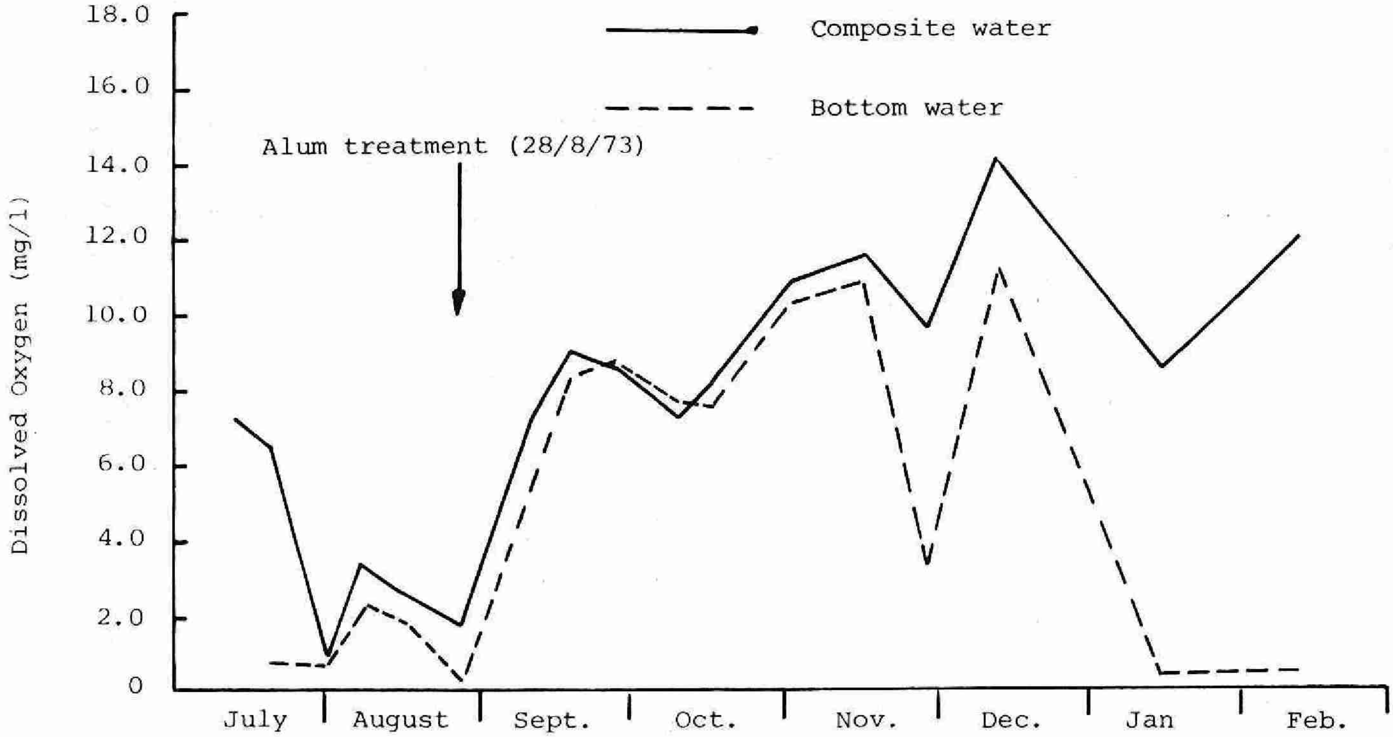
Prior to treatment, anaerobic conditions existed in the bottom waters (Figure 10). Oxygen values above bottom water were also low, averaging only 1.8 mg/l. Following alum treatment, sharp increases in dissolved oxygen content were seen in both the bottom water and the average values for the oxygen profile. It is likely that the removal of decaying organic material from the water coupled with the increase in water transparency causing the stimulation in growth of the macrophytes which in turn produced more oxygen and gave rise to the observed dissolved oxygen increases. Jermelov (1970) and Kennedy and Cooke (1974) stated that improvements in dissolved oxygen conditions were evident following alum treatment due to increases in macrophytic growth. The possibility also exists that wind mixing could have played a role in dissolved oxygen improvements in this particular study. Reduced dissolved oxygen levels in the bottom waters in January and February are probably indicative of increased bacterial activity and decomposition of the precipitated algae and organic material as a result of alum treatment.

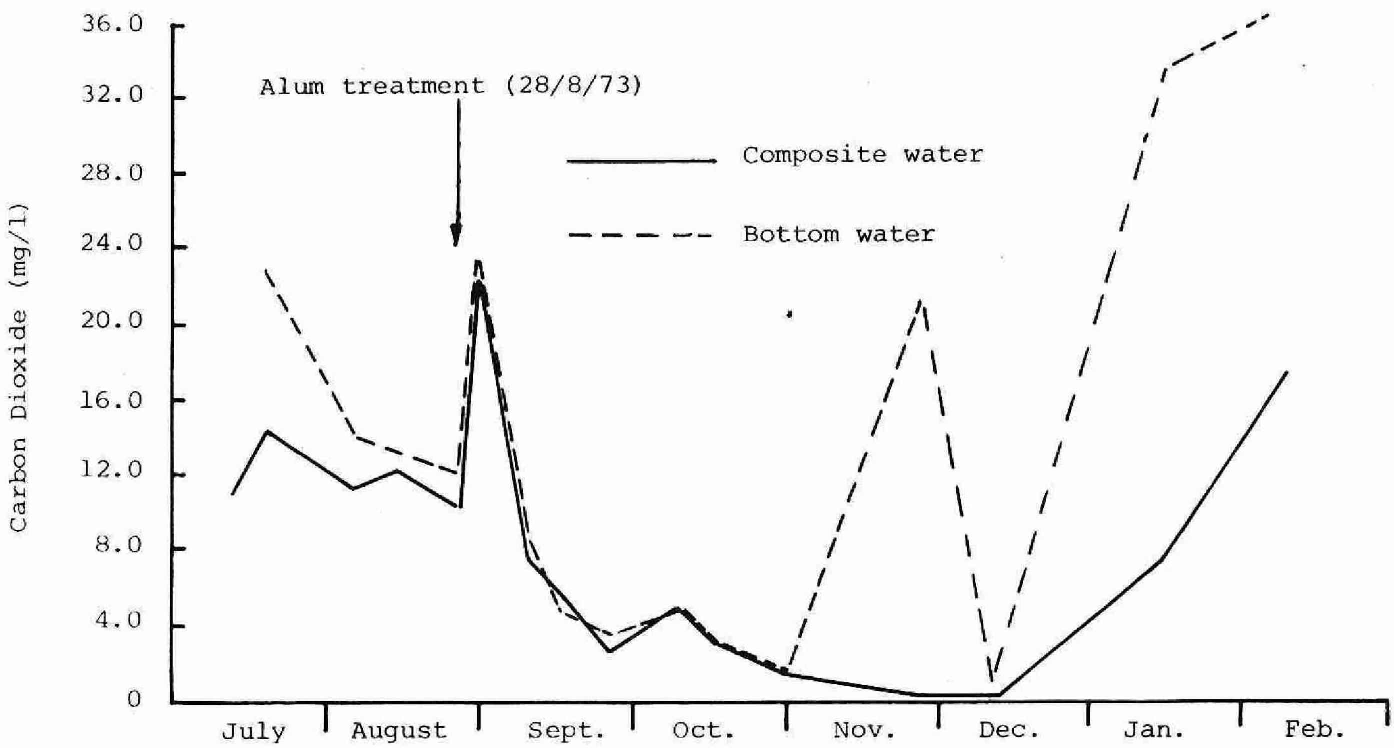
Carbon Dioxide

Increased carbon dioxide content following treatment was observed (Figure 10). The alum application produced an increase in bottom water and composite water CO_2 content from 12.0 and 10.0 mg CO_2/l respectively to 23 mg CO_2/l.

Following this peak, CO_2 levels dropped off quickly. Through the winter months, CO_2 levels increased dramatically. These increases were probably correlated with increases in ammonia associated with decomposition of organic material in the sediment.

FIGURE 10: DISSOLVED OXYGEN AND CARBON DIOXIDE BEFORE AND AFTER ALUM TREATMENT.





Sulphate

As would be expected, the dissociation of aluminum sulphate upon application increased the sulphate content (Figure 11). From a pre-treatment concentration of 17 mg/l sulphate values took a dramatic increase to a maximum value of 123 mg/l as SO_4. Bottom water sulphate values did not show as large an increase but a definite "lag" was seen relative to the composite values. The high increase in sulphate seen in the representative composite samples was immediately followed by a sharp drop in sulphate content suggesting that some of the sulphate was being precipitated out of solution. The process of precipitation of the suphate was probably responsible for the corresponding increase in concentrations in the bottom water during this short period.

The presence of H_2S in bottom water samples taken in January to April may have indicated the possibility that sulphate was being reduced to hydrogen sulphide under anaerobic conditions.

Aluminum

Figure 12 shows aluminum values for composite and bottom water before and after alum treatment. Prior to treatment the pond was characterized by rather high levels of aluminum. The bottom water line demonstrates a peak in aluminum concentration of 3.7 mg Al/l following treatment. Due to sampling irregularities a similar peak was not evident for composite water. It is evident from this graph that aluminum concentration following treatment decreased with time to levels much lower than were measured prior to treatment. It is highly probable that "resident" aluminum was bound in some type of organic form and that addition of aluminum sulphate and subsequent formation of aluminum hydroxide may have precipitated out the organically bound aluminum to yield concentrations less than "background" aluminum values.

Figure 11: SULPHATE BEFORE AND AFTER ALUM TREATMENT.

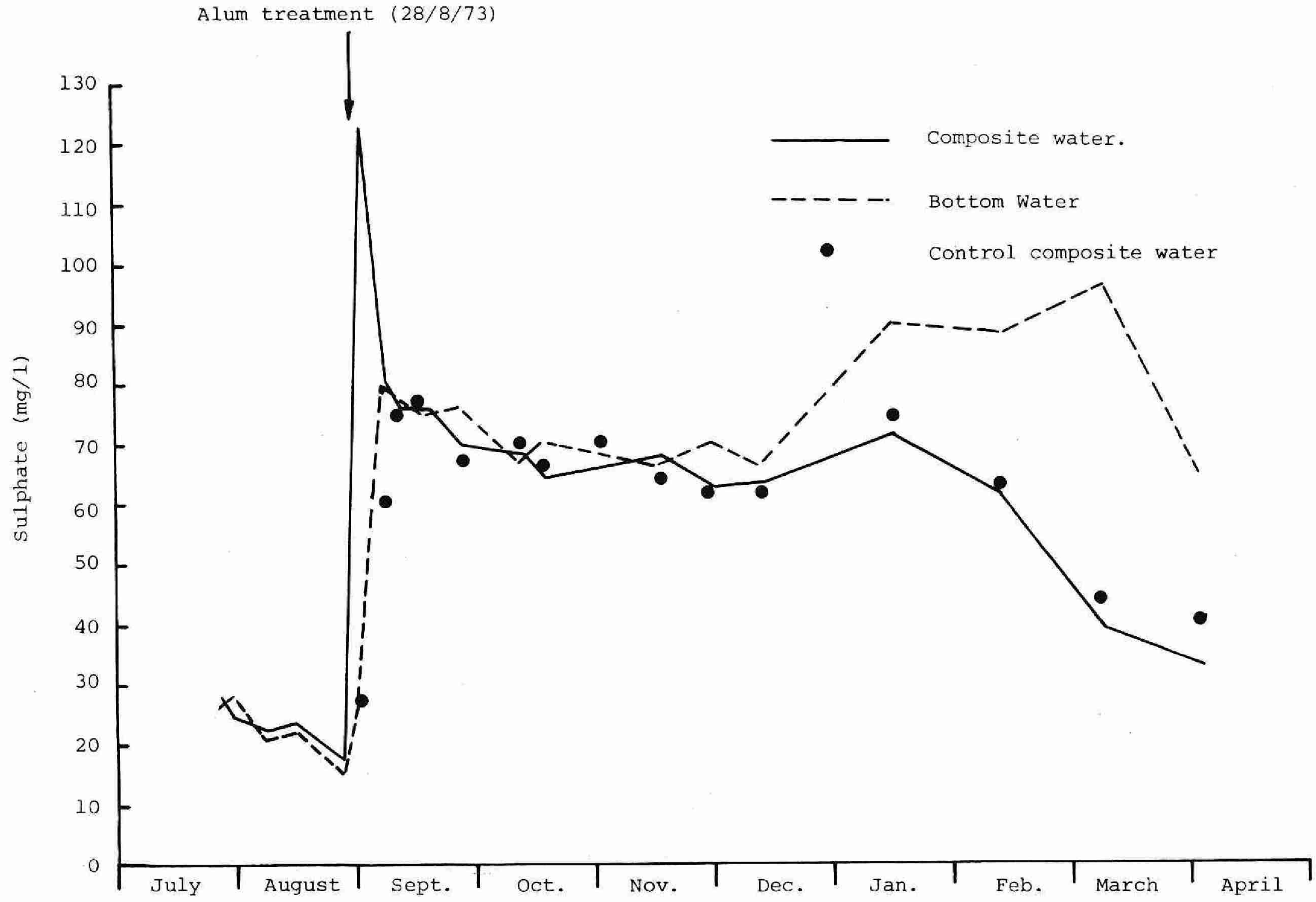
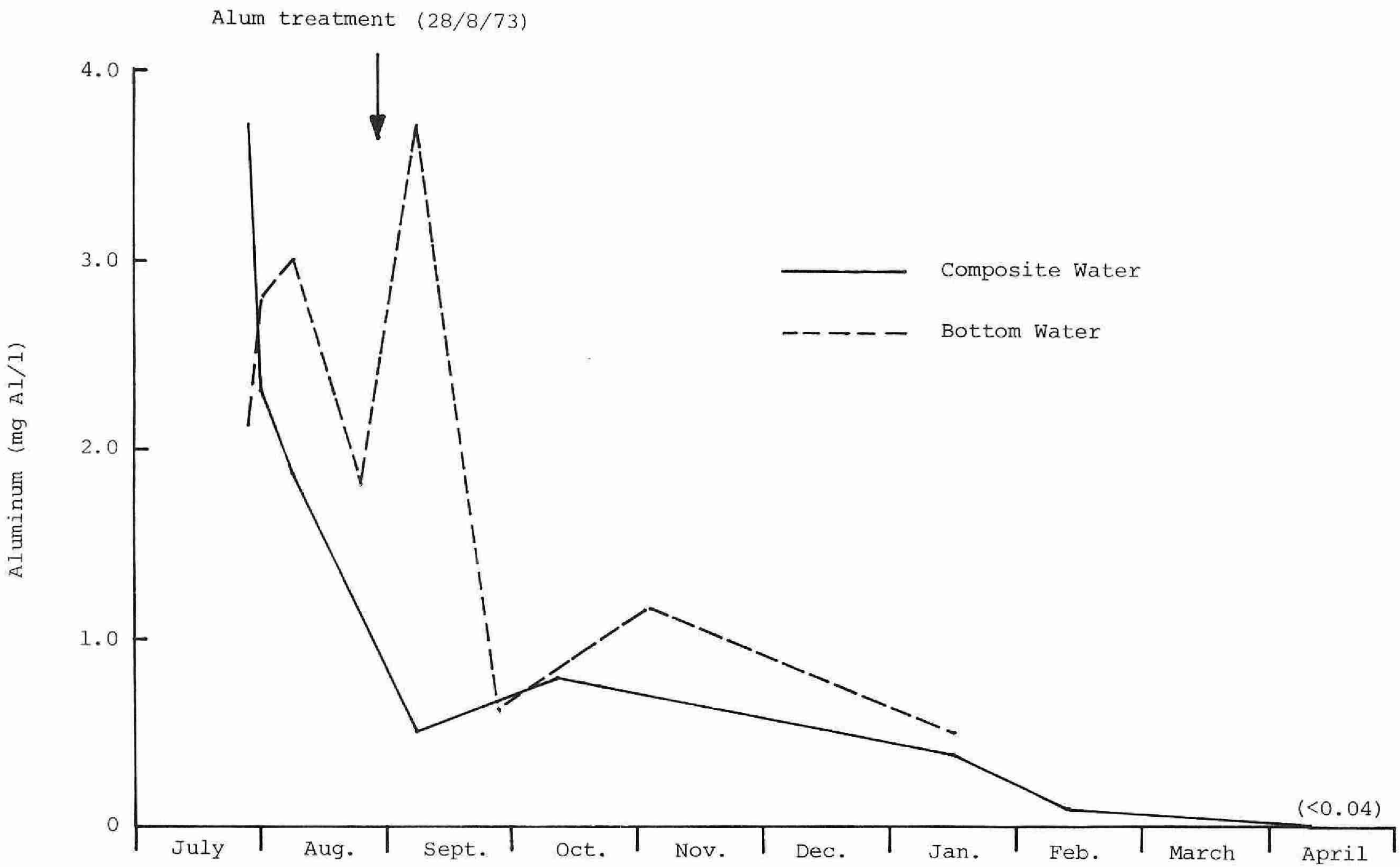


FIGURE 12: ALUMINUM BEFORE AND AFTER ALUM TREATMENT



MOIRA LAKE NUTRIENT INACTIVATION FEASIBILITY STUDY

SITE DESCRIPTION

Moira Lake is located in Huntingdon Township in the County of Hastings approximately 1.6 kilometers south of the Village of Madoc (Figure 13).

The lake is divided into two basins separated by a natural narrows directly south of the Village of Madoc. The mean depth of the combined sections of the lake is approximately 5 meters with the maximum depth being approximately 11 meters. The west basin has a maximum depth of 7.2 meters. The immediate watershed of the lake covers an area of 590 km^2. Two major inlets empty into the west basin, Deer Creek and the Moira River. Moira River drains a large swampy area containing a few small lakes. Due to excessive weed and algal growths, recreational usage has been limited to boating and fishing.

The shoreline of Moira Lake is weed-developed with the exception of the northwest and southwest shore of the west basin.

Due to the experimental nature of alum treatment in natural water bodies it was decided to conduct an enclosure study rather than a whole-lake study at this point. The site chosen for the enclosure study was on the south shore of the west basin in a small cove located approximately ¼ mile from the mouth of the Moira River. The enclosures were installed in approximately 3 meters of water.

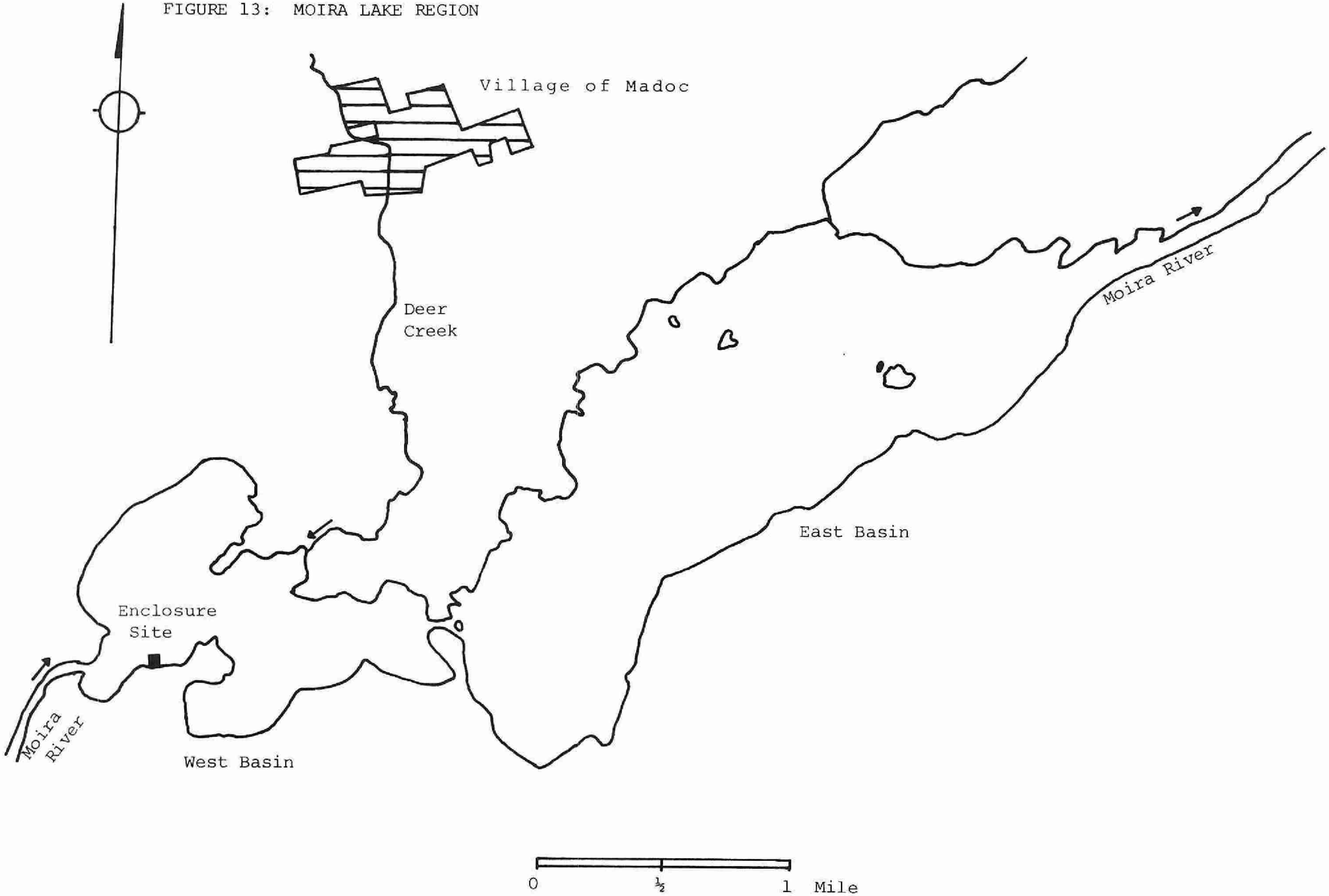
METHODS

Raft and Tube Construction

Open-ended heat-sealed cylinders measuring 6.5 m in length and 1.0 meters in diameter were fabricated from stock rolls of 6 mil. clear polyethylene. These tubes were slipped over a supporting ring structure and attached to a sand-filled large diameter plastic ring which acted as an anchor.

The raft to support the polyethylene enclosure was constructed of 2" x 4" lumber in such a manner that it could be disassembled for easy transport and then reassembled in the field. Flotation for the raft was provided by three styrofoam buoyancy billets.

FIGURE 13: MOIRA LAKE REGION



The raft was assembled and positioned by means of six vertical and four diagonal anchors.

Tube Installation

The tube structures were lowered into the water and the anchor rings were pushed one to two feet into the sediment with the aid of SCUBA. The other end of the tube was pulled through and clamped to collar devices attached to the raft thus enclosing a volume of lake water approximately 2.6 m high and 1.0 meters in diameter continuous with the sediment and the atmosphere. One day was allowed for the suspended sediment to settle. Prior to sampling, inspection of the tubes revealed that they were flaccid, consequently lake water was pumped into the tubes until they were turgid. This allowed for more accurate estimation of enclosed water volumes. The final enclosure water volumes were estimated to be approximately 2.04 m^3.

Sampling Techniques

Secchi disc readings were taken using a 23 cm. black and white disc. Dissolved oxygen profile measurements were made at the surface, 1.5 m and the bottom using the Winkler method. Additions of manganese sulphate and alkalide azide were made in the field. Sulphuric acid reagent and titrations with sodium thiosulphate were carried out in the laboratory.

Representative composite samples were taken in each of the enclosures and the lake using the bilge pump apparatus described in the M.T.R.C.A. pond study methods. In order to obtain a representative composite sample from the surface to the bottom in the enclosures and the lake, volumes of water taken from each stratum were proportional to the volume of that stratum. Water samples were taken at 0.5, 1.5 and 2.5 m representing 1.0 meter strata. This water was pumped into a common vessel, stirred and poured into sample bottles.

Chlorophyll samples were preserved in the field with 1 ml of a 2% suspension of magnesium carbonate. Algal samples were preserved with sufficient Lugol's solution to impart a dark orange colour to the water. Samples for nutrient analysis were immediately placed in coolers containing ice. Samples for heavy metal analysis were fixed with 10 drops of nitric acid in the field. All samples were then transported to the Ministry of the Environment, Laboratories Branch in Toronto for analysis. All analyses were done in accordance with "Outline of Analytical Methods,

Ontario Ministry of the Environment, 1974".

Surface samples were taken at the mouth of the Moira River and Deer Creek.

Jar Test Procedures

The appropriate alum dosage was determined by applying alum in slurry form with concentrations of 40, 50, 75, 100, 150 and 200 mg alum/l to a duplicate series of 8l. jars containing surface water from Moira Lake (two additional jars containing Moira Lake water acted as controls). Coagulation, flocculation and precipitation occurred. Aliquots from both jars which received the same alum concentration treatment were siphoned off into a common container, thoroughly stirred and decanted into sample bottles and submitted for biological and chemical analysis.

Alum Application

Based on a 100 mg/l alum concentration four bags containing 204.0 grams of dry alum each were prepared. At the study site, water was collected from an enclosure and 204 grams of alum was added and stirred until a slurry was formed. The slurry was then poured into the enclosure and stirred to ensure uniform distribution. This procedure was done on four of the eight enclosures.

Enclosure Scheme

Eight enclosures were installed in all. Treatment of these enclosures were as follows:

1. Two enclosures denoted by T_1T_2 were treated with a 100 mg/l dose of alum. Discharge additions were made on a weekly basis (see Discharge Addition Section for details).

2. Two enclosures (A_1A_2) were treated with a 100 mg/l dose of alum. No discharge additions were made to these tubes.

3. Control enclosures C_1 and C_2 were not treated with alum but did receive discharge additions on a weekly basis.

4. Control enclosures C_3 and C_4 were not treated with alum nor did they receive discharge additions.

Discharge Additions

In order to simulate true lake conditions in alum-treated enclosures T_1T_2 and control enclosures C_1C_2, volumes of water from Moira River and Deer Creek were added according to the formula;

$$\text{Discharge Addition} = \frac{VE}{VL} \times VF$$

VE = Volume of enclosure (ft^3)

VL = Volume of lake (west basin ft^3)

VF = Volume of Moira River and Deer Creek discharge in a seven days period (ft^3).

Appropriate volumes of surface water were collected from Moira River and Deer Creek and placed in a large plastic vat. The correct volumes were then added to the enclosure while the same volume of water was simultaneously being pumped out of the enclosures at a lower depth utilizing a 360 g.p.h. electric bilge pump.

Using this method the effect of discharge additions on alum treatment permanence could be seen.

In order to determine volumes of discharge water to be added to the enclosures mean monthly discharges from 1965 to 1973 were calculated (data taken on Moira River at Deloro). The discharge (ft^3) for one week (7 days) was then calculated from this data and incorporated into the aforementioned formula. A Ministry of the Environment Recreational Lakes Report (1972) stated that "the west basin is fed 90% by the Moira River and 10% by Deer Creek". This assumption was implemented to calculate discharge volume for Deer Creek. It was determined that for the months of August 40.8 l. of Moira River water and 4.5 l. of Deer Creek water would have to be added to each of four enclosures every seven days. In September 20.4 l. of Moira River water and 2.3 l. of Deer Creek was added to each of the four pertinent enclosures.

RESULTS AND DISCUSSION

Jar Tests

Phosphorus

The pre-treatment total phosphorus level in the control jars was 44 µg P/l. With the exception of a total phosphorus value of 43 µg P/l with an alum dose of 50 mg/l there was a progressive decrease in total

phosphorus levels with an increase in alum concentration (Figure 14). Maximum total phosphorus removal was achieved with an alum concentration of 200 mg/l and corresponded to a 91% (44 to 4 μg P/l) removal.

Dissolved reactive phosphorus values decreased with an increase in alum dose. A 100 mg/l alum concentration removed 89% (27 to 3 μg P/l) of dissolved reactive phosphorus. Alum concentrations of 150 and 200 mg/l removed 96% (27 to 1 μg P/l) dissolved reactive phosphorus.

Alkalinity

Alkalinity values decreased in an almost linear fashion with an increase in alum dosage (Figure 14). A 200 mg/l alum application resulted in 69% (119 mg/l to 37 mg/l as $CaCO_3$) reduction in alkalinity. A 100 mg/l alum application resulted in a 36% reduction in alkalinity (119 mg/l to 76 mg/l as $CaCO_3$). This corresponded to a 62% efficiency when compared to the hypothetical alkalinity reduction.

pH

Reductions in pH were observed with an increase in alum concentration. A 200 mg/l alum dose resulted in a pH decrease from a control value of 8 to a pH of 7 (Figure 15).

Sulphate

As would be expected, increases in sulphate concentrations were noted with an increase in alum concentration. A 100 mg/l alum application resulted in a sixfold increase in sulphate concentration from a control value of 10 mg/l to 60 mg SO_4/l. Compared to a hypothetical increase of 48 mg SO_4/l the observed increase of 50 mg SO_4/l represents a 100% efficiency.

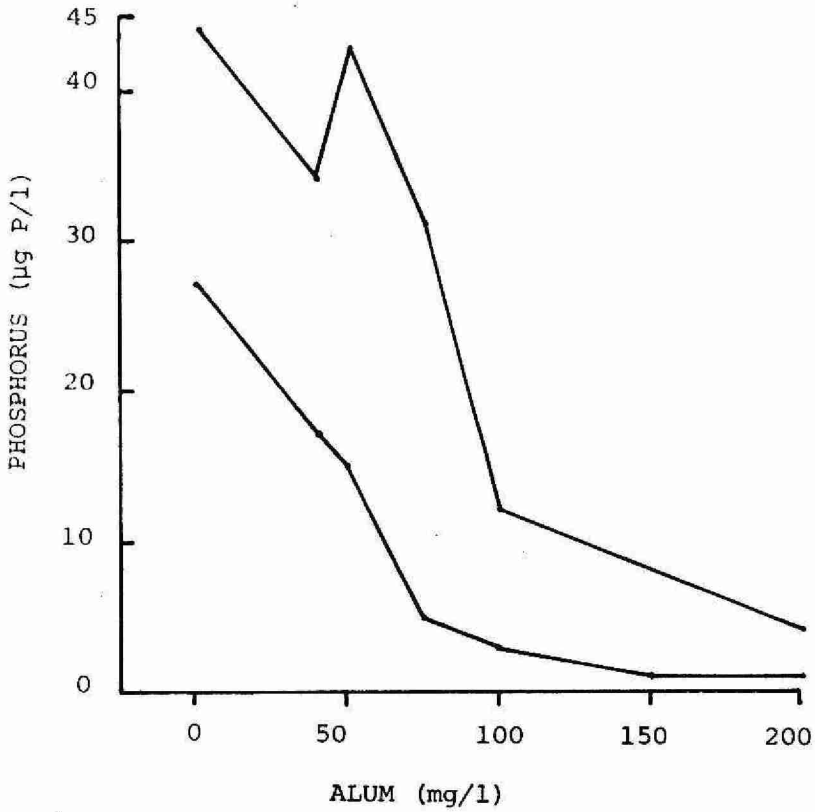
Algae

Figure 16 demonstrates the algal removal efficiency of alum. An alum concentration of 40 mg/l had no effect on algal removal but from alum concentrations of 50 mg/l to 200 mg/l significant percentage removals were noted.

An application of 200 mg/l alum resulted in an overall algal removal of 96% (from a control value of 892 a.s.u./ml to 39 a.s.u./ml). Dominant blue-green algae (specifically *Oscillatoria*) were reduced by 95%. Flagellates were reduced by 94% while green algae and diatoms experienced a 100% removal

FIGURE 14: JAR TEST RESULTS

PHOSPHORUS AND ALKALINITY REDUCTIONS



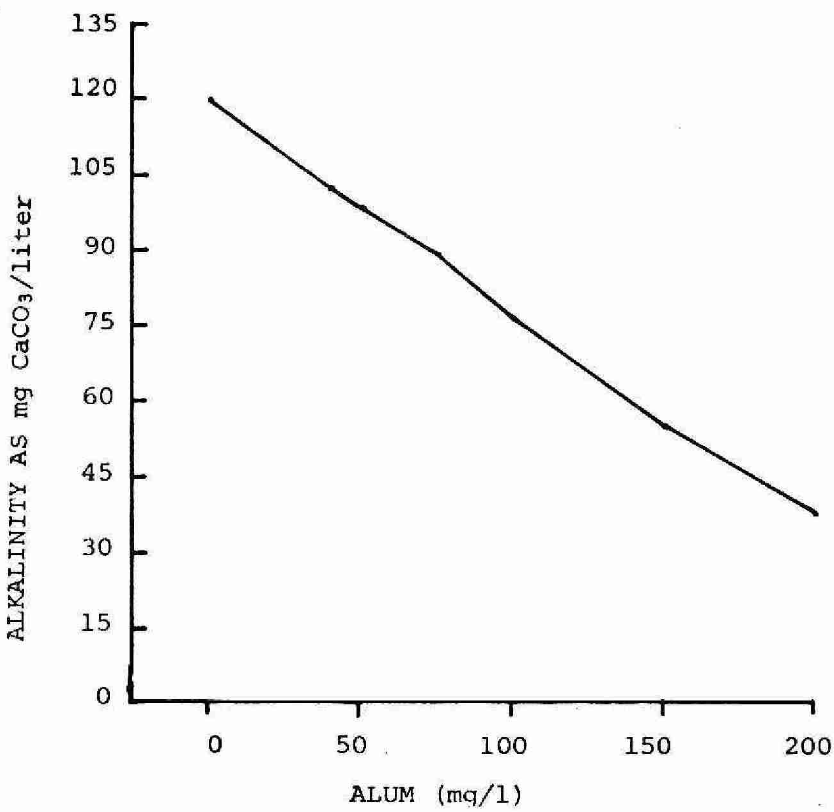
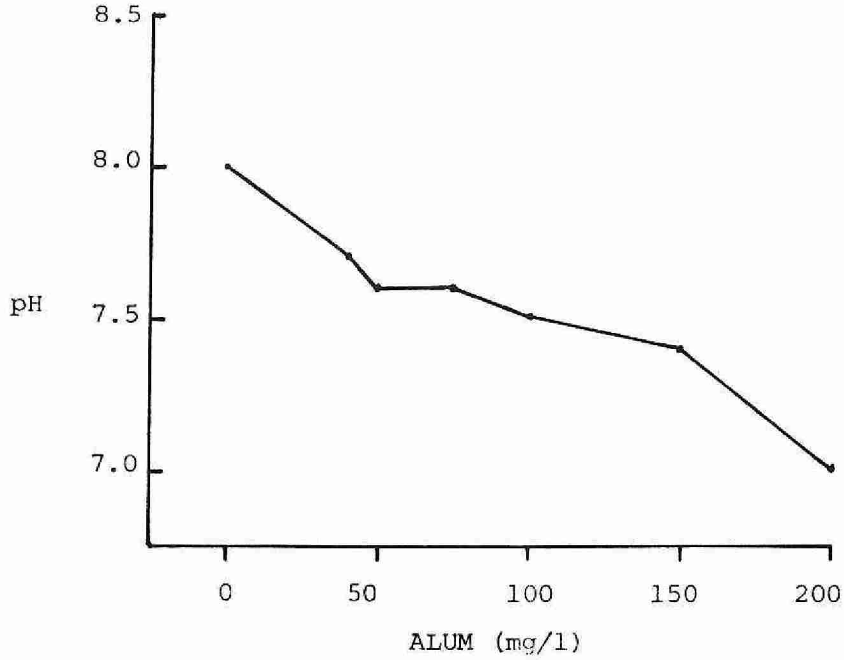


FIGURE 15: JAR TEST RESULTS -

pH AND SULPHATE



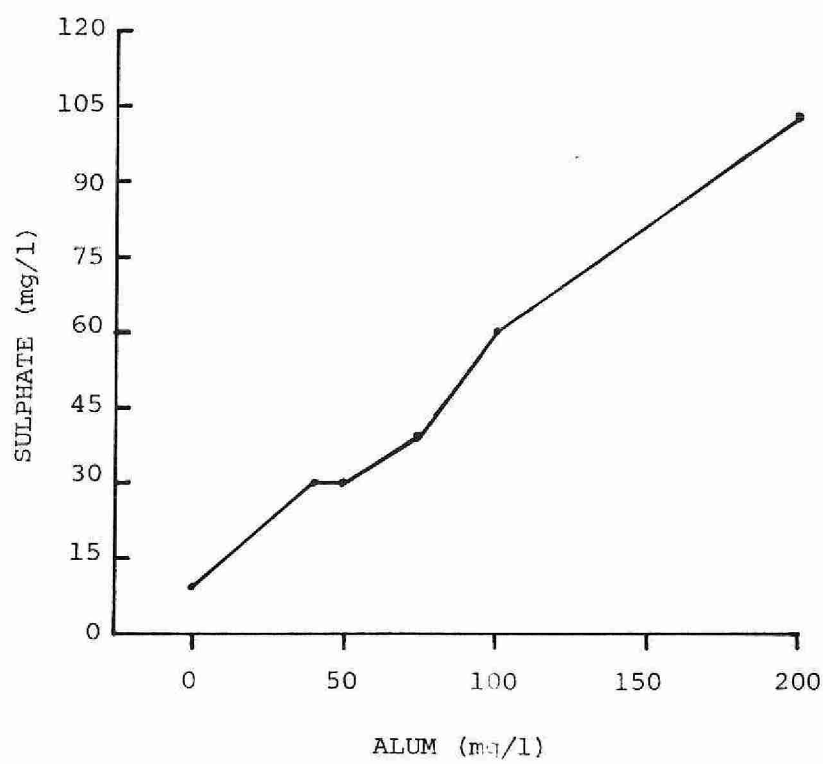
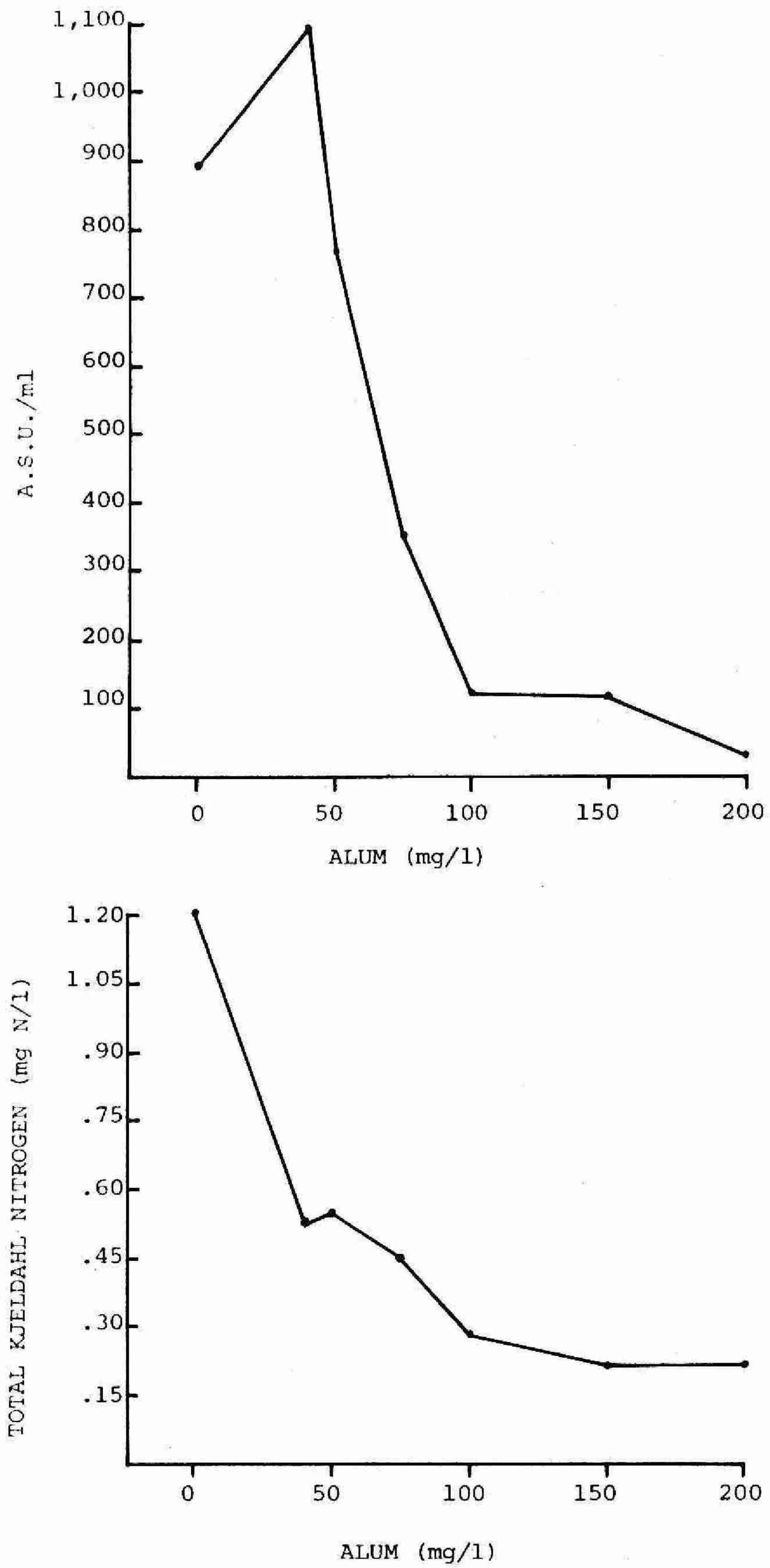


FIGURE 16: ALGAL AND TOTAL KJELDAHL NITROGEN REMOVAL



at an alum concentration of 200 mg/l. In terms of relative removal efficiencies alum was most effective in removing green algae, diatoms, then blue-green algae and flagellates in that order.

Total Kjeldahl Nitrogen

Figure 16 shows reductions in Total Kjeldahl Nitrogen following alum treatment. Maximum Kjeldahl nitrogen removal was achieved at an alum concentration of 150 mg/l and represents an 82% removal (1.2 to 0.21 mg N/l). This nitrogen removal can be partially correlated with aforementioned algal removal rates.

Based on these jar replicate test results it was decided that a 100 mg/l alum dose was sufficient to remove a large percentage of nutrients and yet not create extreme increases in sulphate concentrations or decreases in pH and alkalinity. A 100 mg/l alum dose resulted in:

1) a 73% reduction in total phosphorus (from 44 to 12 μg P/l).
2) a 89% reduction in dissolved reactive phosphorus (from 27 to 3 μg P/l).
3) a 77% reduction in total Kjeldahl nitrogen (from 1.2 mg/l to 28 mg N/l).
4) a 36% reduction in alkalinity from a control of 119 to 76 mg/l as $CaCO_3$.
5) a 93% reduction in the phytoplankton standing stock (from 892 to 126 a.s.u./ml).
6) a reduction of 0.5 pH units from a control of 8.0 to 7.5.
7) an increase in sulphate concentration from a control value of 10 mg SO_4/l to 60 mg SO_4/l.

Time of Application

In order to obtain maximum effectiveness from an alum treatment it is very important to treat the body of water at the appropriate time. Jernelov (1970) has stated that the most appropriate time to apply alum to shallow lakes is in the early spring at the time of ice break-up when the largest amount of "mobile" phosphorus in the aquatic system was in the form of "phosphate". One serious drawback to this statement is that in shallow lakes with large drainage basins the large discharge flow at spring break-up results in a relatively short retention time. It follows that if a lake of this nature is treated with alum in early spring the

permanence of the treatment is greatly reduced. In the case of Moira Lake the heaviest discharge rates were present in early spring (Figure 17). Treatment at this time would have proven to be relatively ineffectual due to a low retention time. In order to prolong treatment permanence it became apparent that the most appropriate time for treatment would be when discharge rates were minimal ie June through to October. As well, dissolved reactive phosphorus levels were more than twice as high immediately prior to enclosure treatment (July 30 - 57 μg P/l) than were seen in early spring (April 25 - 22 μg P/l).

It was felt, therefore, that alum treatment in a period of minimum discharge flow accompanied by high dissolved reactive phosphorus levels would yield optimum results.

Enclosure Integrity

Enclosures $A_{1,2}$ suffered rather large rips soon after their introduction into the lake. This yielded anomalous results throughout the course of experimentation. The other six enclosures remained intact throughout the experiment with the exception of enclosures $C_{1,2}$ which on September 25th succumbed to the activities of muskrats.

Field Results

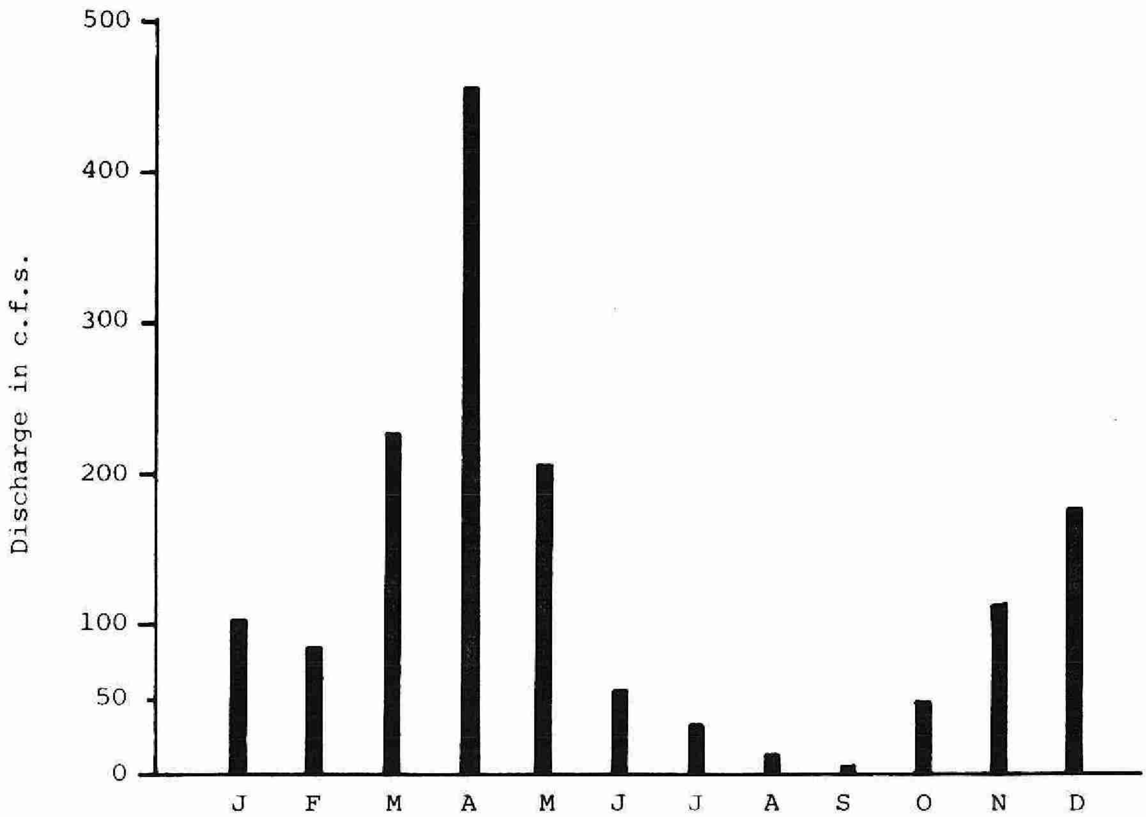
On July 30th slurried aluminum sulphate was introduced to each of enclosures T_1T_2 A_1 and A_2 at a concentration of 100 mg alum/l (see methods section).

Upon addition of the alum a milky colour was immediately imparted to the water. Within 10 minutes floc formation was observed. Within 24 hours precipitation of the floc to the sediments was complete. For all data presented each point represents the mean of two composite values, one value being obtained from each of two enclosures undergoing the same treatment.

Physical and Chemical Parameters

Throughout the course of this experimentation there was no significant variation in either temperature or oxygen profiles between the enclosures or between the enclosures and lake water.

FIGURE 17: MONTHLY MEAN DISCHARGES (c.f.s.) FOR MOIRA RIVER AT DELORO FROM 1965 to 1973.



No Secchi disc readings were taken inside the enclosures for fear of disturbing the floc and/or the highly flocculent sediments. Secchi disc readings in the lake varied from a maximum of 1.3 m to a minimum of 0.9 m. Parameters that were effected as a result of alum treatment were total and dissolved reactive phosphorus, organic and free ammonia nitrogen, alkalinity, pH, conductivity, sulphate, aluminum, BOD, COD, chlorophyll a and phytoplankton standing stocks as well as inorganic and total carbon and arsenic.

As is best exemplified by control enclosures $C_{3,4}$ parameters that were effected by simply enclosing a volume of lake water with polyethylene were total and dissolved reactive phosphorus, phytoplankton standing stocks and chlorophyll a.

CONTAINMENT EFFECTS

As previously stated both alum treatment and enclosure had an effect on identical parameters, namely total and dissolved reactive phosphorus, phytoplankton standing stocks and chlorophyll a. A discussion on the effects of containment is warranted before a proper assessment of the effects of alum can be assessed.

Phytoplankton Standing Stocks

Jordan and Bender (1973) in discussing the effects of containment on a plankton community stated that modification of turbulence, light penetration, nutrient environment and enclosure bacterial growth could substantially effect plankton populations and species dominance as well as productivity.

Lund (1972) noted that following enclosure there was a qualitative difference in the phytoplankton as well as a reduction in the total population. Stoermer, Schelske and Feldt (1971) noted a drastic reduction in phytoplankton populations following enclosure.

In the present study the phytoplankton demonstrated trends that generally concur with the observations of the aforementioned investigators. Quantitatively, the factors mentioned by Jordan and Bender (1973) probably influenced the results seen in Figure 20 . Phytoplankton populations in enclosures $C_{3,4}$ were consistently lower than the rest of the enclosures and the lake. In fact all enclosures exhibited levels lower (to one degree or another) than those seen in the lake. Phytoplankton in enclosures $C_{1,2}$ (discharge water added) were consistently more numerous than those in $C_{3,4}$.

This was probably due to weekly nutrient-laden discharge additions providing increased growth potential and/or the fact that these discharge additions themselves contained substantial phytoplankton populations.

Although there was no large increase or decrease in the quantity of phytoplankton in enclosures $C_{3,4}$ qualitative changes were noted. Following enclosure the diatoms, specifically Rhizosolenia, Stephanodiscus and Fragilaria, underwent a drastic reduction. Levels dropped from 1,296 a.s.u./ml (taken immediately after enclosure) to 103 a.s.u./ml within one week. The diatoms never increased above 50% of the original level of 1,296 a.s.u./ml throughout the experiment. This trend was also seen in the other enclosures to the same extent. It was apparent that diatoms are rather intolerant of containment effects. Populations of green and flagellated algae remained stable while the dominant blue-greens tended to fluorish in all enclosures, whereas chlorophyll production in enclosures $C_{3,4}$ reflects simply containment effects.

It would be expected that with the exception of rainfall additions the amount of dissolved reactive phosphorus in enclosures $C_{3,4}$ would be constant. It would further be expected that some sort of competition would exist between free-floating phytoplankton and attached algal forms for this dissolved reactive phosphorus. Following containment dissolved reactive phosphorus in enclosures $C_{3,4}$ started to drop (Figure 19). There was a corresponding drop in total phosphorus (Figure 18) indicating that in all probability the algae attached to the enclosure walls were successfully competing with the suspended algae for available nutrients.

Lund (1972) observed that following enclosure of Blelham Tarn water chlorophyll a levels were significantly lower as compared to the open lake. A similar trend was evidenced in the present study. Enclosures $C_{3,4}$ had chlorophyll a levels that paralleled but were almost always less than levels in the lake. Enclosures $C_{1,2}$ on the other hand had chlorophyll a levels that were slightly higher than levels in enclosures $C_{3,4}$.

Phosphorus

Following containment both total and dissolved reactive phosphorus in enclosures $C_{3,4}$ dropped (Figures 18and 19). Discharge additions made to enclosures $C_{1,2}$ resulted in phosphorus concentrations that were slightly higher than those seen in enclosures $C_{3,4}$.

The previous discussion has outlined that containment effects can introduce variables and exert stresses on certain parameters that would undoubtedly limit the precision of assessing the effects of alum treatment on water quality. As will be seen, treatment in enclosures demonstrated an effect in terms of water quality, however due to containment effects caution must be exercised in interpreting the results of an *in situ* study of this nature.

FIELD STUDIES

Total Phosphorus

Upon alum application drastic reductions in total phosphorus were seen in both sets of test enclosures (Figure 18).

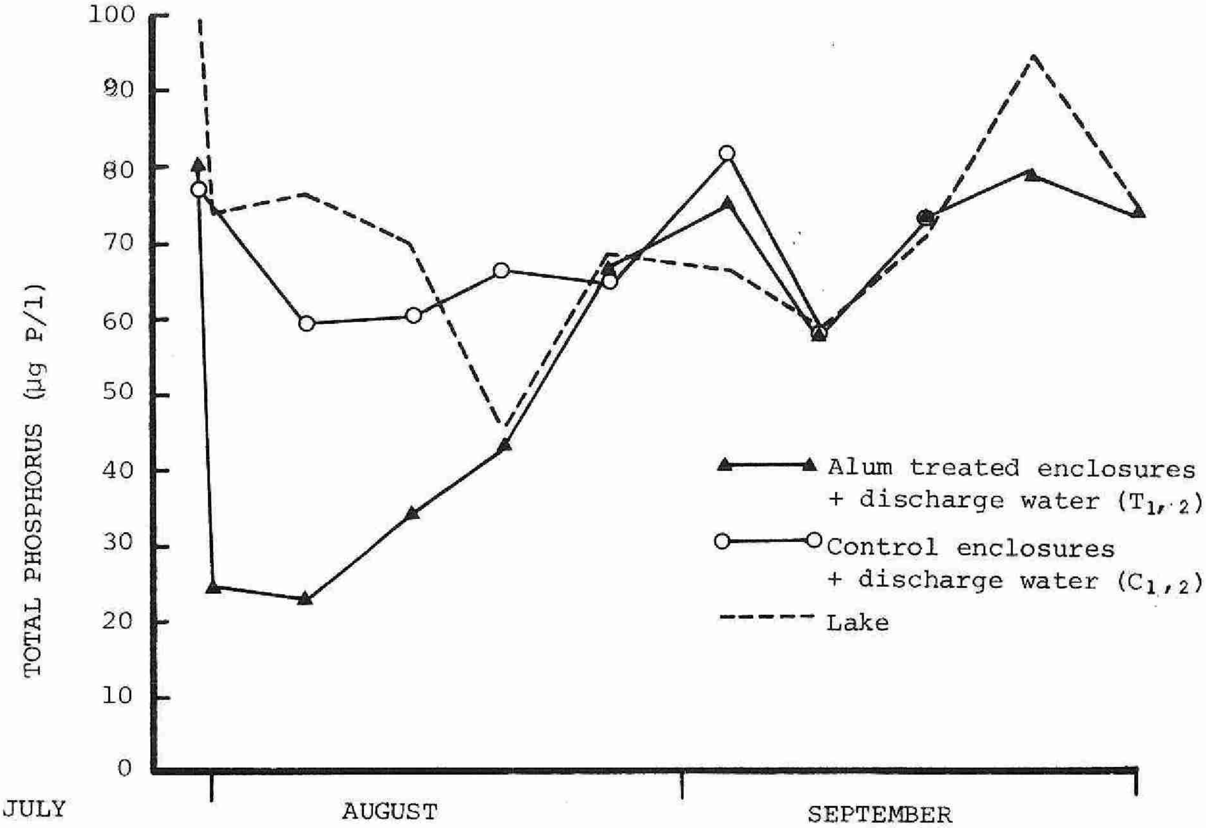
In enclosures $T_{1,2}$ (alum treatment with discharge addition) there was a 70% reduction of total phosphorus from 80 to 24 μg P/l within 24 hours. Following this, levels gradually increased until late August when total phosphorus was once again at control levels. Increases in total phosphorus following initial reduction can be attributed to weekly discharge additions.

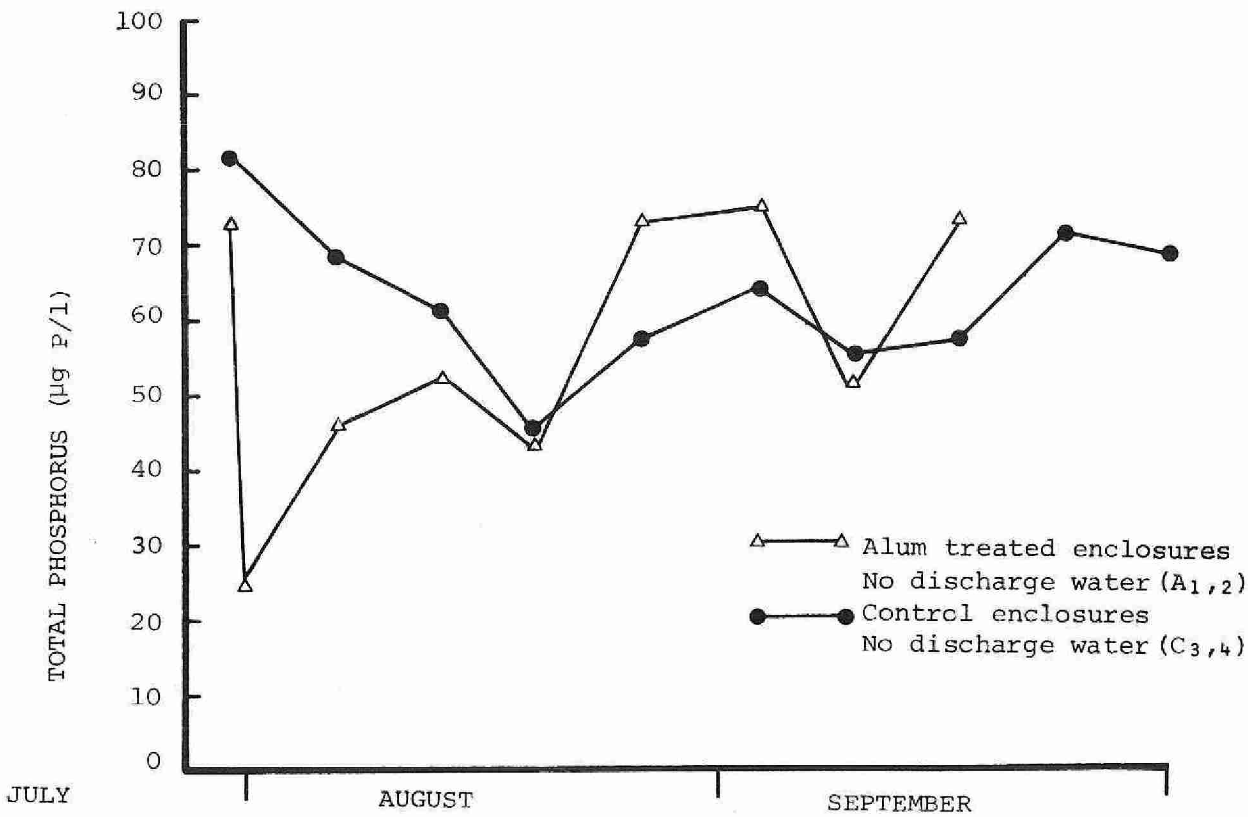
In enclosures $A_{1,2}$ which were treated with alum but had no discharge additions, total phosphorus dropped sharply from a 73 to 24 μg P/l (67% reduction). following this, however, levels increased more rapidly than evidenced in enclosures $T_{1,2}$. It would be expected that since these enclosures received no nutrient-laden discharge water that total phosphorus values would remain well below control levels. As previously discussed and as seen by total phosphorus values for $C_{3,4}$ it would further be expected that enclosure effects would accentuate this trend for levels in $A_{1,2}$. As has been previously stated (section on enclosure integrity) the integrity of these enclosures was in doubt. This fact probably produced the anomalous results.

Large total phosphorus fluctuations in lake water were probably due to the close proximity of the study site to the mouth of the Moira River. River values from week to week were virtually identical to those values obtained from the lake.

Total phosphorus levels in $C_{1,2}$ tended to be higher than those in $C_{3,4}$. This is not surprising since enclosures $C_{1,2}$ received weekly discharge additions whereas enclosures $C_{3,4}$ did not.

Figure 18. TOTAL PHOSPHORUS VARIATIONS IN TEST AND CONTROL ENCLOSURES AND LAKE WATER





Dissolved Reactive Phosphorus

Alum application resulted in a 95% removal of dissolved reactive phosphorus in both enclosures $T_{1,2}$ and $A_{1,2}$. In the case of $T_{1,2}$ levels remained much lower than the controls for an extended period of time. Test enclosure levels did not reach control levels until mid-September. Once again levels in $A_{1,2}$ showed the same trend as seen in total phosphorus values.

Dissolved reactive phosphorus levels in $C_{1,2}$ and $C_{3,4}$ tended to be higher than levels in the open lake for the first month and a half. A corresponding jump in the lake phytoplankton standing crop would suggest that drops in dissolved reactive phosphorus occurred due to the incorporation of same into the plankton organisms. As for the higher levels of phosphorus in the control enclosures along with relatively smaller phytoplankton populations (even in enclosures $C_{1,2}$) it is possible that containment was exerting an inhibiting influence on the assimilation of readily available phosphorus by the phytoplankton thus rendering phytoplankton populations much smaller than seen in the lake (Figure 20).

Phytoplankton

Preliminary jar tests indicated that an alum concentration of 100 mg/l was very efficient in terms of algal removal (Moira Lake Nutrient Inactivation Feasability Study - Jar Test Results). In enclosures $T_{1,2}$ and $A_{1,2}$ alum application removed 76 and 63% of the algae respectively. (Figure 20). Phytoplankton standing stocks in enclosures $T_{1,2}$ demonstrated a gradual increase after their initial reduction and were at control levels (approx. 60.0 x 10^2 a.s.u./ml) within 13 days. Following this, levels in $T_{1,2}$ were always significantly higher than either sets of controls but with the exception of one sampling date never exceeded levels in open water. Both sets of controls tended to show increases in phytoplankton standing stocks with time but relative to lake and test enclosures were always smaller. Control enclosures $C_{3,4}$ showed the least increase with enclosures $C_{1,2}$ being only slightly higher despite weekly discharge additions. On both enclosures $T_{1,2}$ and $A_{1,2}$ alum treatment resulted in a substantial initial reduction in both green and blue-green algae (predominantly *Ulothrix* and *Anabaena* respectively), however, within a period of two weeks increases in total phytoplankton standing stocks were attributed to significant come-backs of both green and blue-green algae with the blue-green *Anabaena* dominating. Further increases through the last half of

Figure 19. DISSOLVED REACTIVE PHOSPHORUS VARIATIONS IN TEST AND CONTROL ENCLOSURES AND LAKE WATER

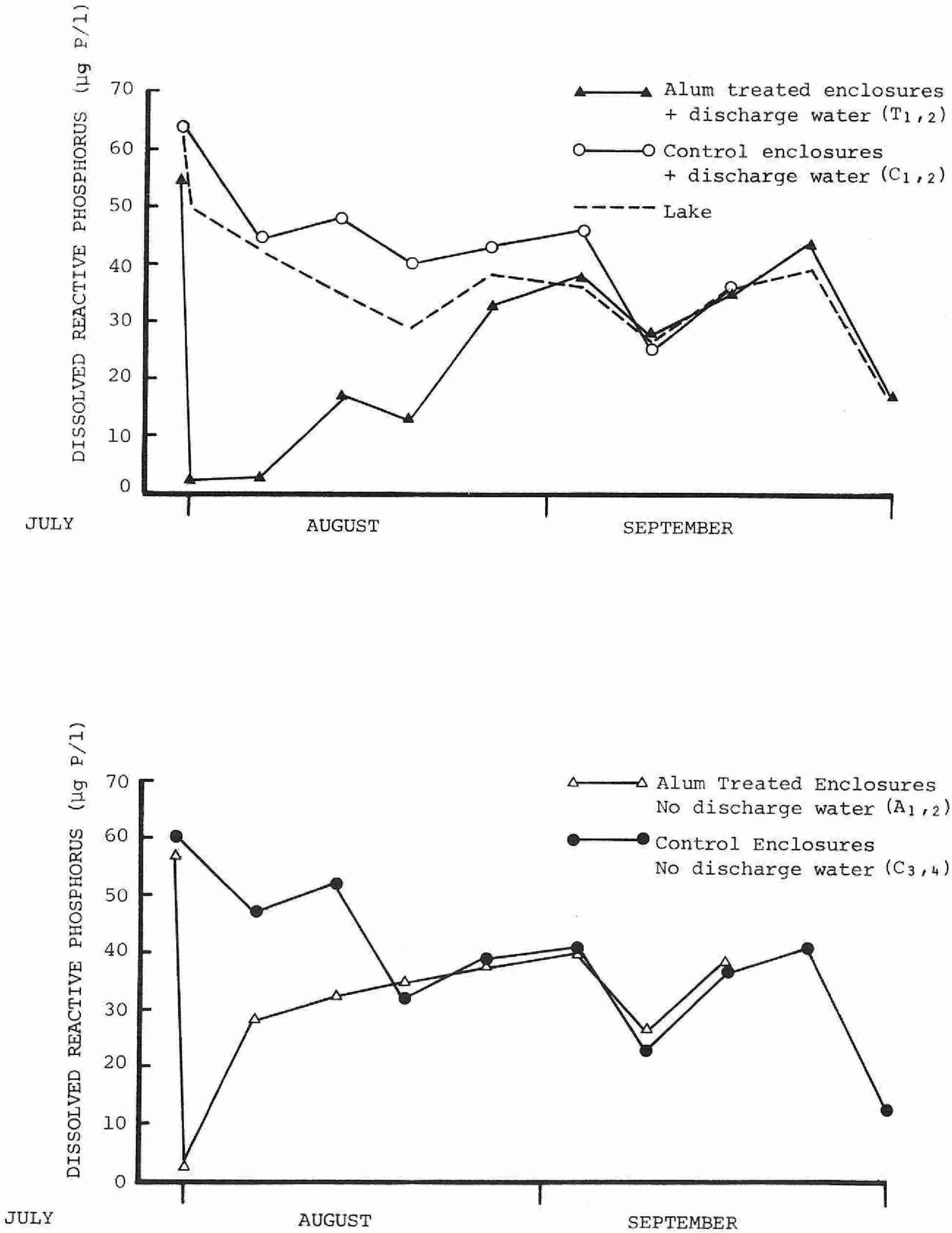
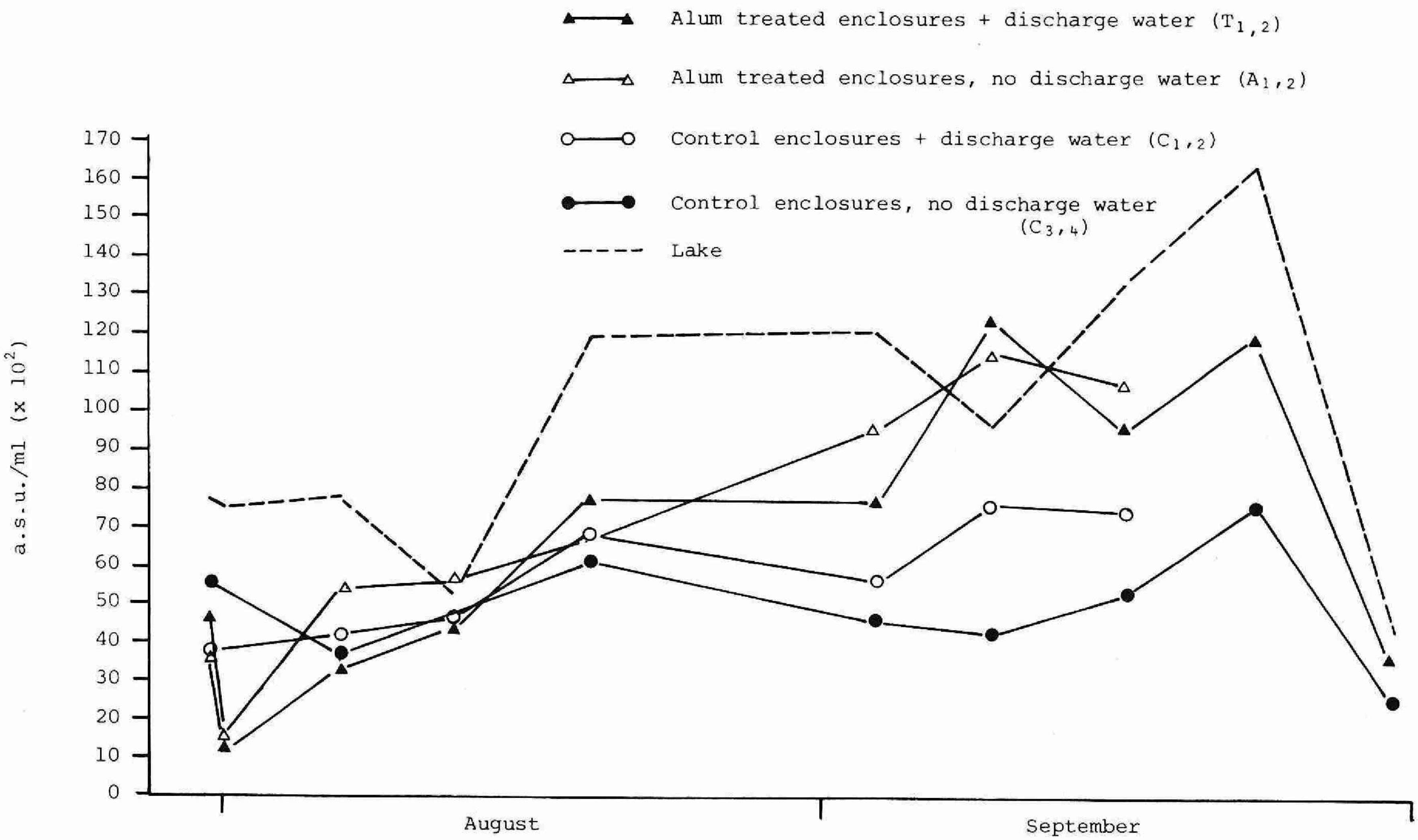


FIGURE 20: EFFECT OF ALUM TREATMENT ON PHYTOPLANKTON STANDING STOCKS



August and all of September were a result of huge increases in the blue-green alga Anabaena as well as equivalent increases in Oscillatoria and Microcystis. Although increases in blue-greens were evident in enclosures $C_{1,2}$ and $C_{3,4}$ they were not of the magnitude witnessed in test enclosures $T_{1,2}$ and $A_{1,2}$.

It is difficult to assess why enclosures T_1T_2 should have phytoplankton standing stocks that were higher than that seen in enclosures $C_{1,2}$ since both sets of enclosures received exactly the same discharge additions each week. It is plausible to assume that the effect of alum treatment on parameters such as total and dissolved reactive phosphorus, pH, CO_2 content, colour, turbidity or ammonia levels could in turn effect the environment of the existing phytoplankton in such a manner as to yield phytoplankton standing stocks much higher than those seen in enclosures that did not receive alum treatment over a period of time.

For this type of study the yardsticks of assessing the effect of alum treatment are essentially phytoplankton standing stocks and phosphorus concentrations. The results presented demonstrated that although alum was effective in the removal of both algae and phosphorus these results were not long lasting. Under the experimental conditions it was also evident that the use of in situ polyethylene enclosures presented certain difficulties in being able to accurately predict alum treatment longevity. The reduction of light transmittance by the polyethylene walls coupled with the presence of attached algae on these walls resulted in an environment that was only an approximation to lake conditions. The results for phytoplankton standing stocks and total and dissolved reactive phosphorus indicated that although alum treatment effects could be seen, containment effects introduced a variable that acted like alum treatment itself ie. reductions in algae and phosphorus. Extrapolating to a whole lake treatment based on the results of in situ studies would yield results that would represent an overestimation of the longevity of alum treatment. It would be expected that a whole lake treatment would show both phosphorus and phytoplankton levels returning to pre-treatment conditions much faster than the in situ studies indicated.

Lund (1972) demonstrated that by essentially closing off a volume of Blelham Tarn water from inflow effects the water thus enclosed showed improvements in chlorophyll, phosphorus and water clarity tending towards oligotrophy compared to lake water. This phenomenon was also

observed in the present study in enclosures $C_{3,4}$ and demonstrates that if the source of enrichment is removed, improvements in water quality results.

Chlorophyll a

Following alum treatment enclosures $T_{1,2}$ and $A_{1,2}$ showed rapid drops in chlorophyll a levels. (Figure 21). Within the first week drops in chlorophyll a concentrations were witnessed in control enclosures $C_{1,2}$ and $C_{3,4}$ as well as the lake; thus, drops in chlorophyll a levels in control enclosures could not be ascribed to containment effects. Although considerable variations were evident it became apparent that chlorophyll a levels in $C_{3,4}$ tended to be consistently lower than levels in enclosures $C_{1,2}$ and $T_{1,2}$ which received discharge additions. The trend in $C_{3,4}$ concurs with the correspondingly low levels of phytoplankton and dissolved reactive and total phosphorus seen in the same enclosures.

Chlorophyll levels in enclosures $T_{1,2}$ were for the most part slightly lower than lake values but tended to parallel the latter.

Nitrogen

Upon alum treatment test enclosures $T_{1,2}$ and $A_{1,2}$ exhibited marked reductions in ammonia nitrogen (Figure 22). In enclosures $T_{1,2}$, for instance ammonia nitrogen experienced a reduction of 82% (from .28 to .05 μg N/l). Ammonia concentrations in $T_{1,2}$ showed a gradual increase followed by a sharp increase in mid-August to control and lake levels. Enclosures $C_{3,4}$ had ammonia levels that were usually higher than lake levels and can be attributed to the accumulation of this waste product within the enclosures. Enclosures $C_{3,4}$ on the other hand had ammonia levels that were generally lower than levels in the other enclosures and the lake. It is difficult to assess why this should be so but two possibilities exist. Enclosures $C_{3,4}$ did not receive discharge additions and as such would not receive weekly ammonia doses as exhibited by late August peaks in enclosures $C_{1,2}$. Also nitrate values in all enclosures were very small (usually less than .01 mg N/l) throughout the course of the experiment. The possibility exists that periphyton on the enclosure walls may have been assimilating free ammonia thus "pulling" it out of solution and accordingly yielding the smaller ammonia levels in these enclosures. Hutchinson (1957) states that some investigations have found that fresh water algal species utilize nitrate in preference to ammonia but that ammonia can be used as a nitrogen source. Hutchinson

FIGURE 21: CHLOROPHYLL a VARIATIONS IN TEST AND CONTROL ENCLOSURES AND LAKE WATER

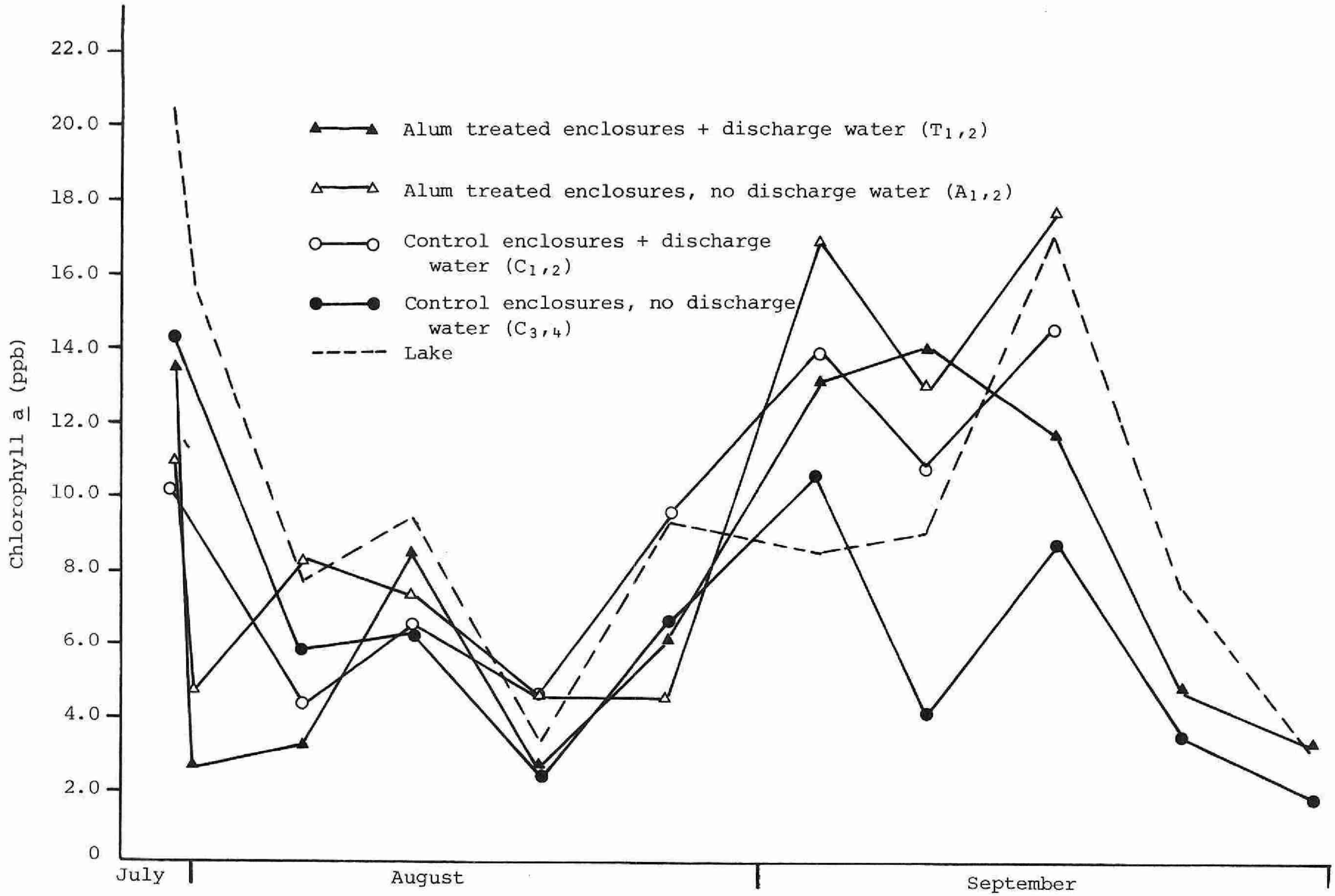
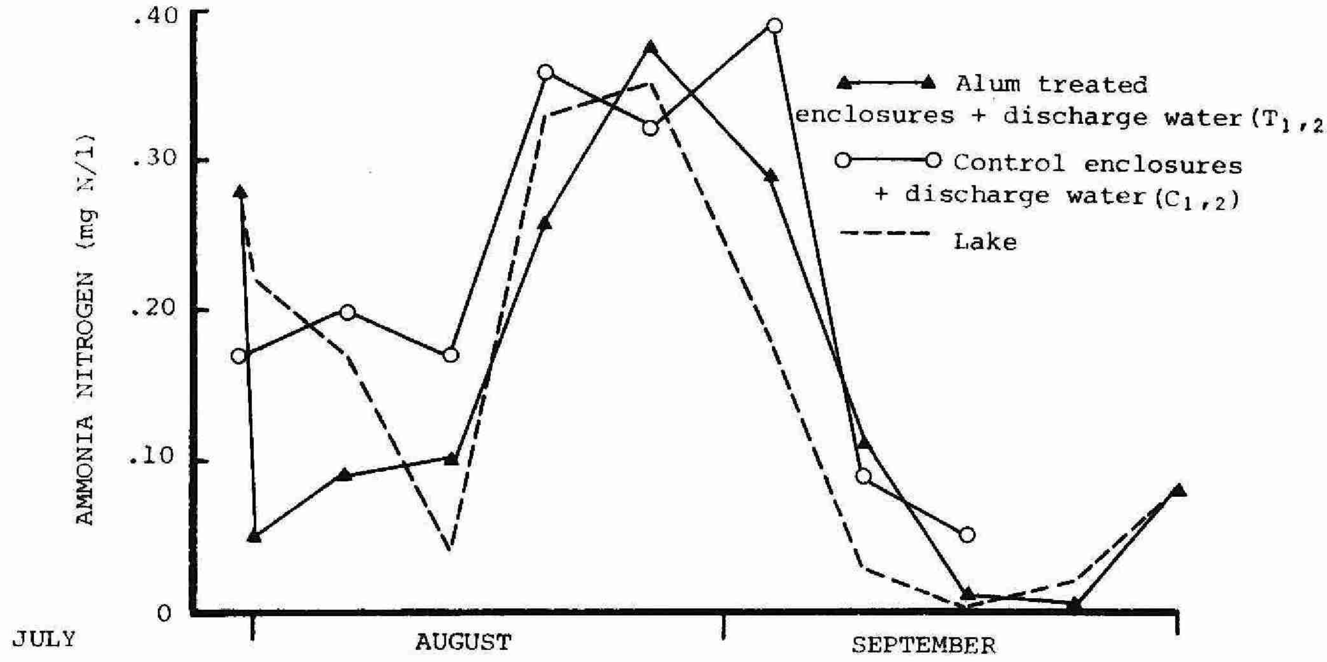


FIGURE 22: VARIATIONS IN AMMONIA NITROGEN IN TEST AND CONTROL ENCLOSURES AND LAKE WATER



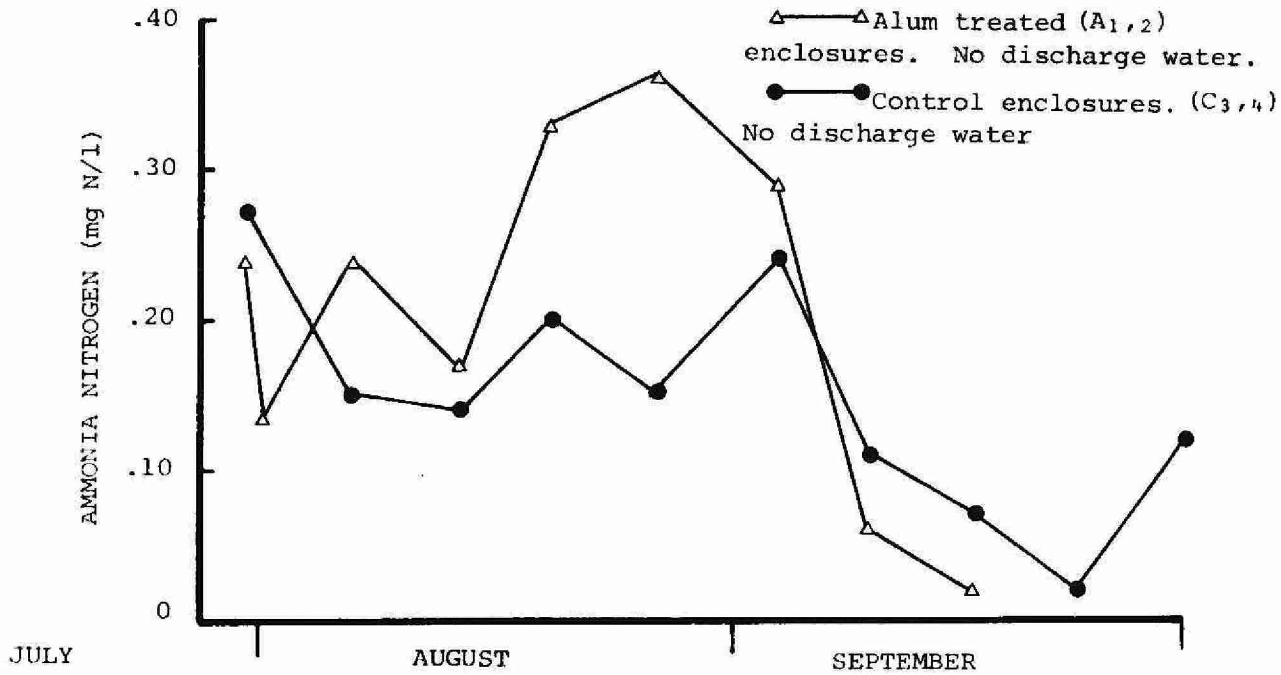
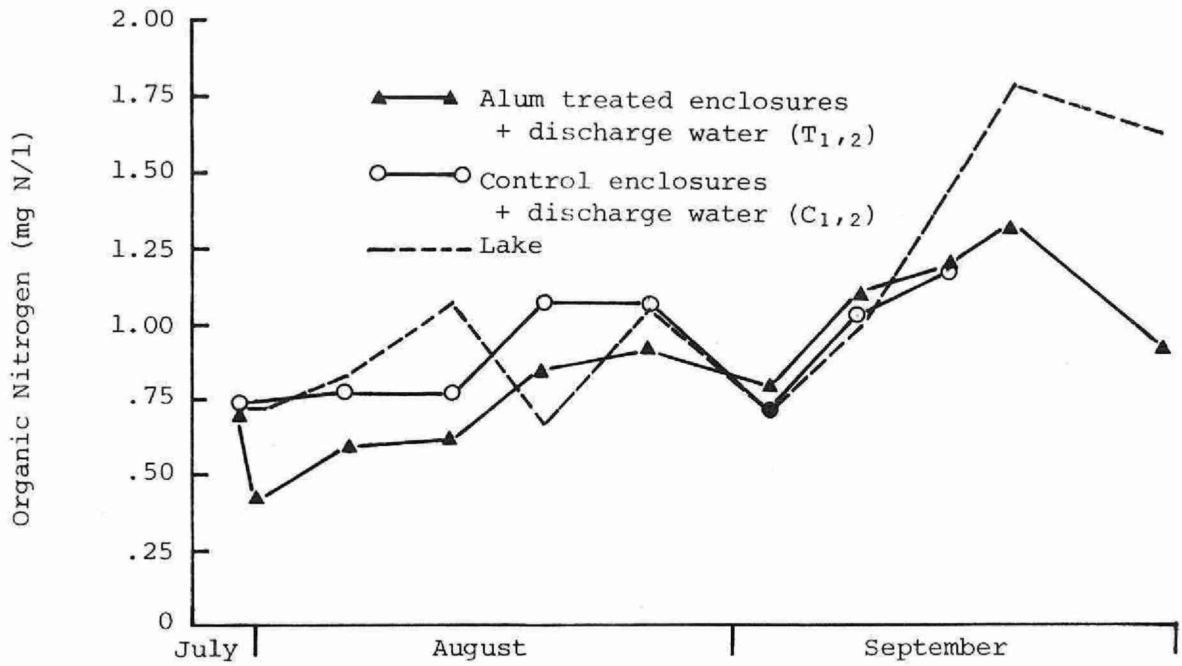
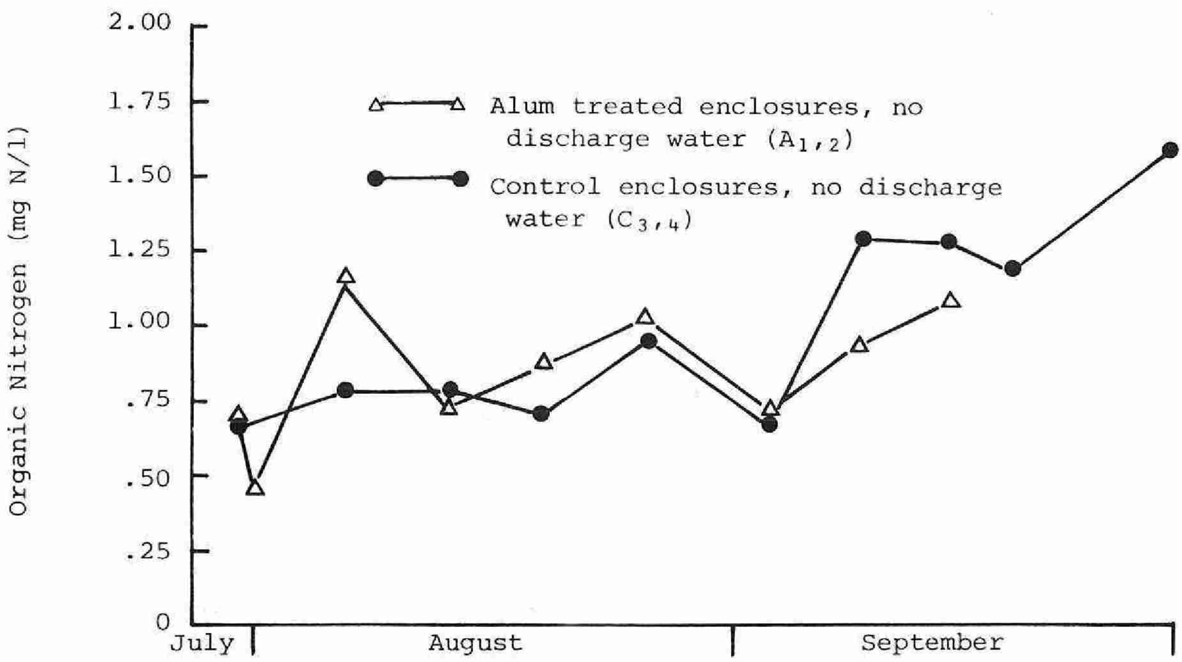


FIGURE 23: VARIATIONS IN ORGANIC NITROGEN IN TEST AND CONTROL ENCLOSURES AND LAKE WATER





goes on to state that "there is little doubt that part of the ammonia present in lake waters can be bound to colloidal particles". The large reductions in ammonia shown in enclosures $T_{1,2}$ were probably a result of the physical enmeshment of the ammonia bound to the colloid by the aluminum hydroxide floc and subsequent precipitation out of the water column.

Figure 23 shows that some loss of organic nitrogen was evident in enclosures treated with alum. Enclosures $T_{1,2}$ showed a reduction of 39% from 70 to 43 mg N/l. Although free and colloidal organic nitrogen were probably also precipitated out the drops in organic nitrogen can, in part, be correlated to corresponding drops in the phytoplankton standing crop (Figure 20).

Alkalinity

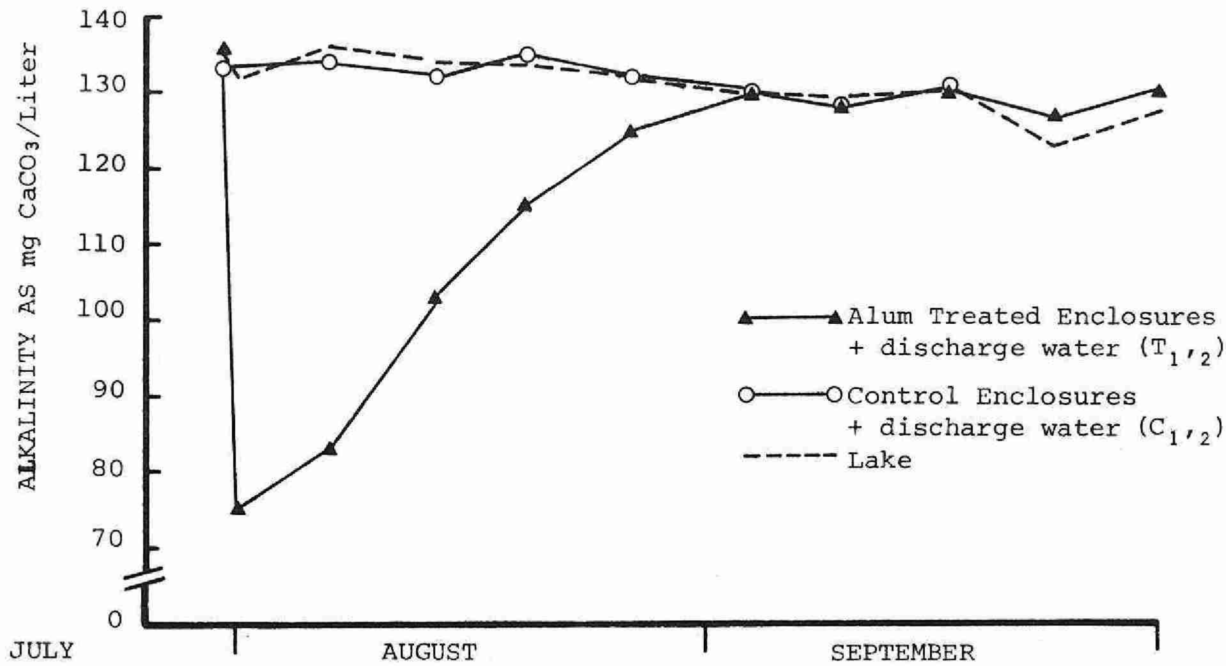
As was seen in the M.T.R.C.A. Study, alkalinity drops approximately 0.5 mg/l as $CaCO_3$ for every 1.0 mg of alum added. In enclosures treated with alum, this same trend was evident. Relative to hypothetical alkalinity reduction there was an 85% efficiency noted. Alkalinity dropped from 136 to 75 mg/l as $CaCO_3$ in enclosures T_1T_2 and over time demonstrated a gradual return to levels in control enclosures and lake water. (Figure 24). Alkalinity levels in enclosures $A_{1,2}$ demonstrated the usual anomolous trends. No significant variation in alkalinity was seen in any one set of control enclosures or between control enclosures and lake water.

pH

Since the hydrolysis of aluminum salts tends to lower pH, the results in Figure 25 are not surprising. Enclosures $A_{1,2}$ showed a sharp reduction in pH from 7.8 to 7.3 while enclosures $T_{1,2}$ showed a more gradual lowering of pH to levels much lower than evidenced in the former enclosures (from a pretreatment value of 7.9 to a low of 6.6 on August 13th). Hereafter pH increased to control levels rather quickly.

Craig (1975) in studying the effect of depressed pH on the American flagfish (Jordanella floridae) concluded that any depression in pH would adversely affect egg production, frequency of spawning, spawning size, fertility of the eggs, possibly hatching success, fry survival and growth. In the present study there was a noted pH depression that could possibly adversely affect a resident fish population assuming the entire lake was to be treated with alum. Craig's study

FIGURE 24. VARIATIONS IN ALKALINITY IN TEST AND CONTROL ENCLOSURES AND LAKE WATER



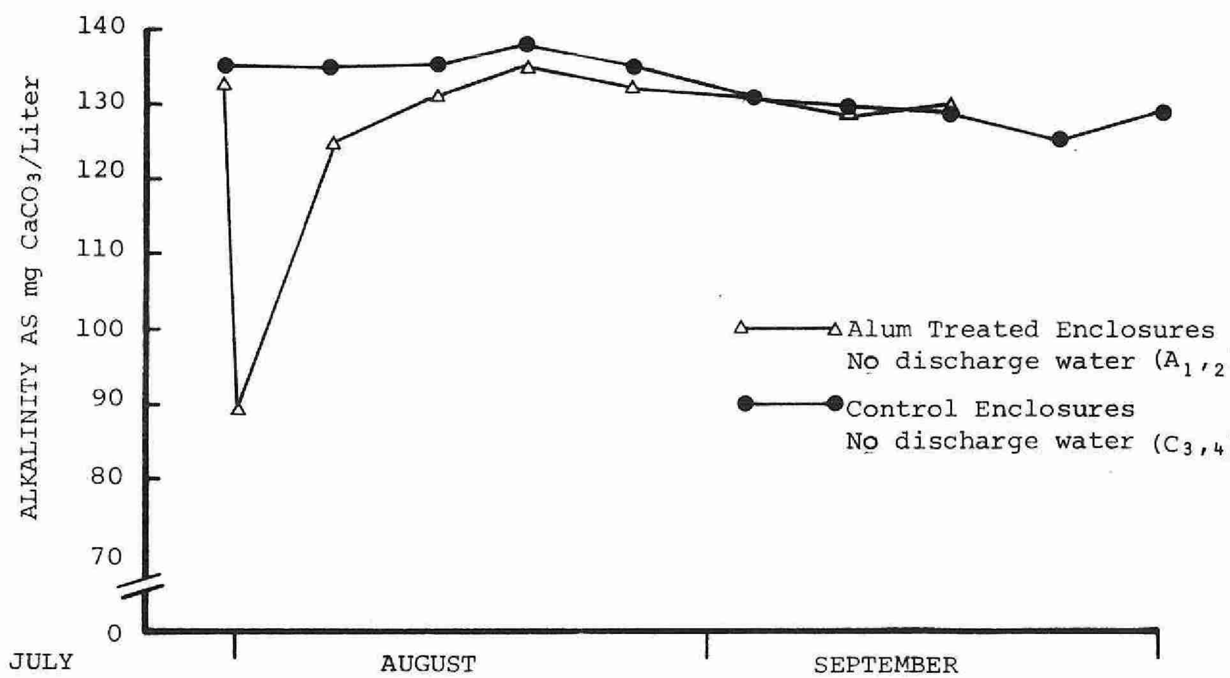
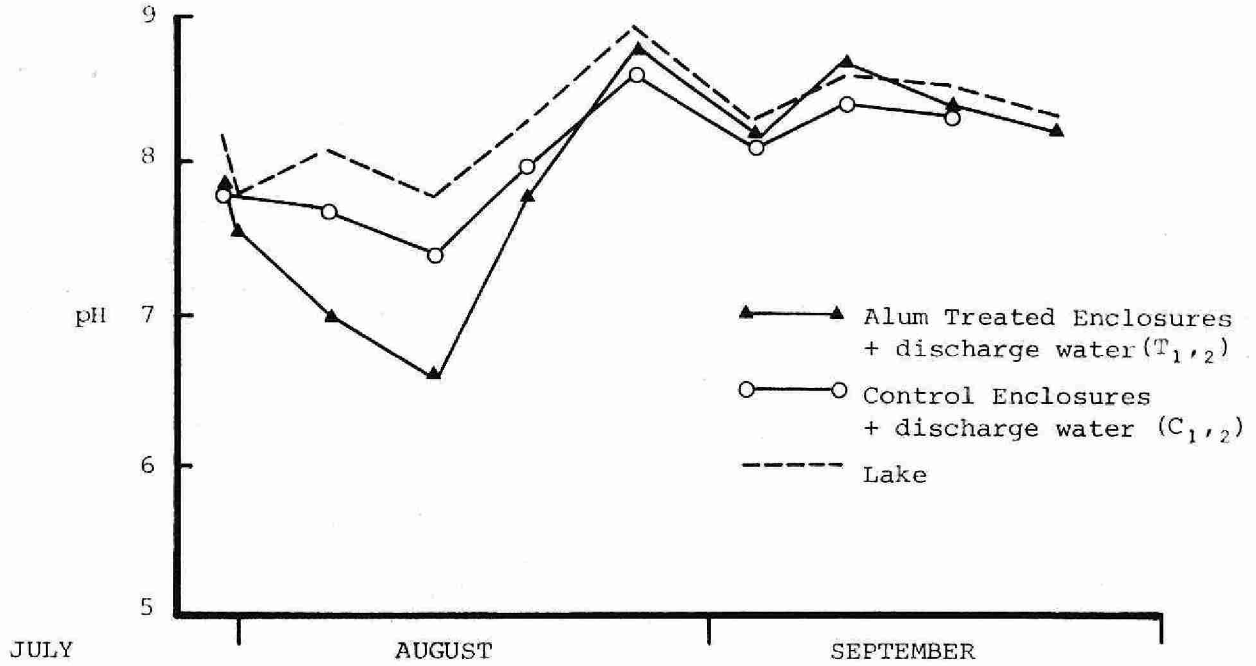
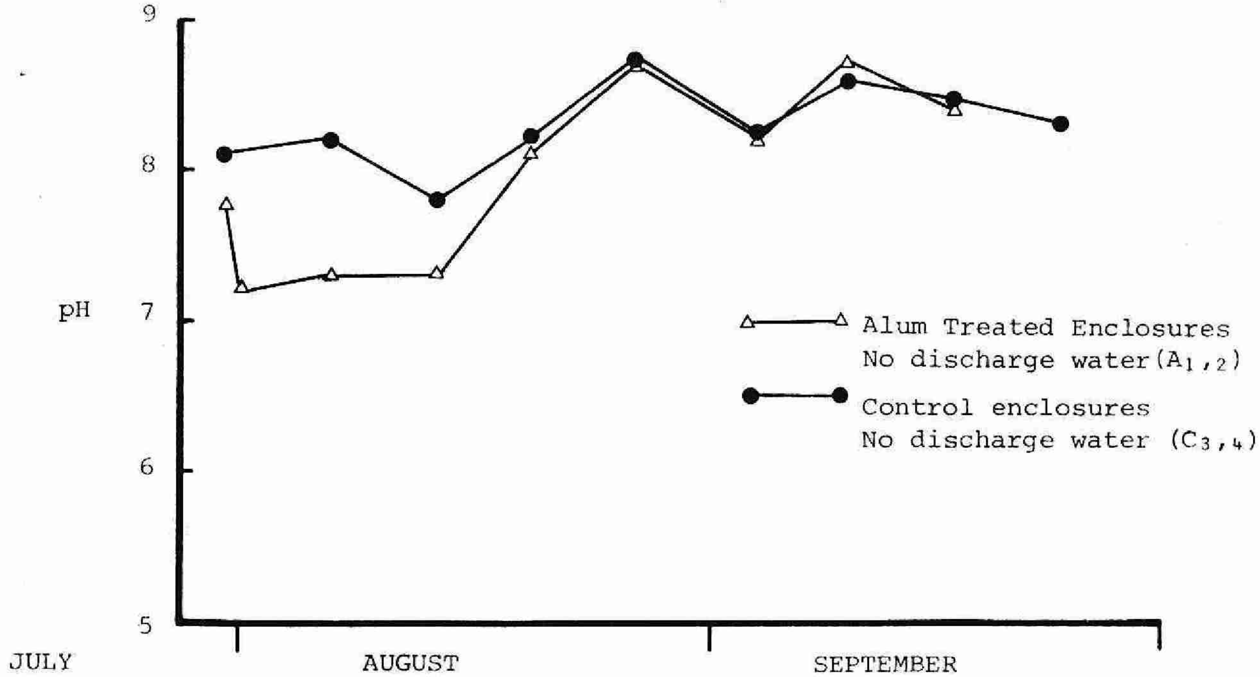


FIGURE 25. pH VARIATIONS IN TEST AND CONTROL ENCLOSURES AND LAKE WATER





dealt with pH values ranging from 6.8 to 4.5 whereas this study dealt with a pretreatment pH of 7.9 to a post treatment low of 6.6. It is unlikely that this pH reduction would have any lethal or sub-lethal effects.

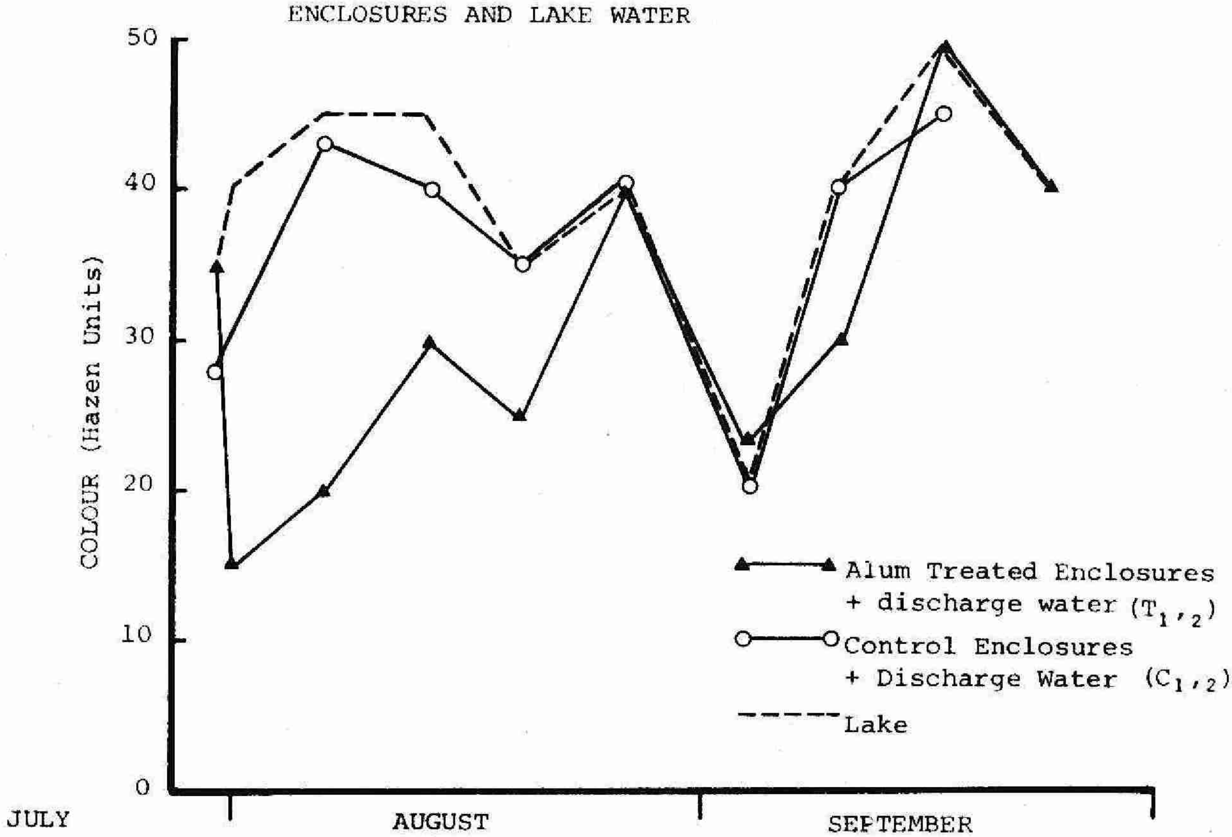
Colour

Colour in natural water is the result of the presence of hydrophilic colloids (Cohen and Hannah 1971). Alum has been shown to significantly reduce colour in natural waters (Landner and Jernelov, 1970, Peterson et al, 1973) and thereby induce an improvement in the overall aesthetics of the water. Figure 26 shows that following alum treatment there were significant reductions in colour in enclosures $T_{1,2}$ (from 35 to 15 Hazen Units) and in enclosures $A_{1,2}$ (from a mean of 33 to 20 Hazen Units). Within 26 days, however, colour values in enclosures $T_{1,2}$ were back to control and lake levels.

Arsenic

Historically, Moira Lake has had an arsenic problem as a result of contamination from the Deloro Smelting and Refining Company located upstream from the lake. Owen and Galloway (1969) observed that samples collected from the river below Deloro and from Moira Lake had arsenic concentrations of 0.28 and 0.16 p.p.m. respectively. They stated that although the Deloro Smelting and Refining Company had implemented control measures, arsenic levels below Deloro represented significant contamination in view of the O.W.R.C. objective of 0.05 p.p.m. In the present study arsenic levels were monitored in the enclosures following alum treatment with the results seen in Figure 27. In both enclosures $T_{1,2}$ and $A_{1,2}$ arsenic values dropped from pretreatment levels of 0.9 and .11 mg/l respectively to levels less than 0.03 mg/l. Arsenic levels in enclosures $T_{1,2}$ went from less than 0.03 back to control and lake levels in 25 days. Ferguson and Louis (1972) in reviewing the arsenic cycle in natural waters, stated that arsenic may exist in either organic (bonded to sulphur and carbon in organic compounds) or inorganic forms. As well, arsenic may be accumulated by aquatic organisms. It is, therefore, likely that the addition of a trivalent metal such as aluminum could precipitate arsenic bound in organic or inorganic forms. Although there is no data to substantiate it, the possibility that phytoplankton in the enclosures may have contained significant fractions of arsenic and that a significant portion of the algae was precipitated out by alum treatment could explain in part the drastic reductions in arsenic levels following treatment.

FIGURE 26. COLOUR VARIATIONS IN TEST AND CONTROL ENCLOSURES AND LAKE WATER



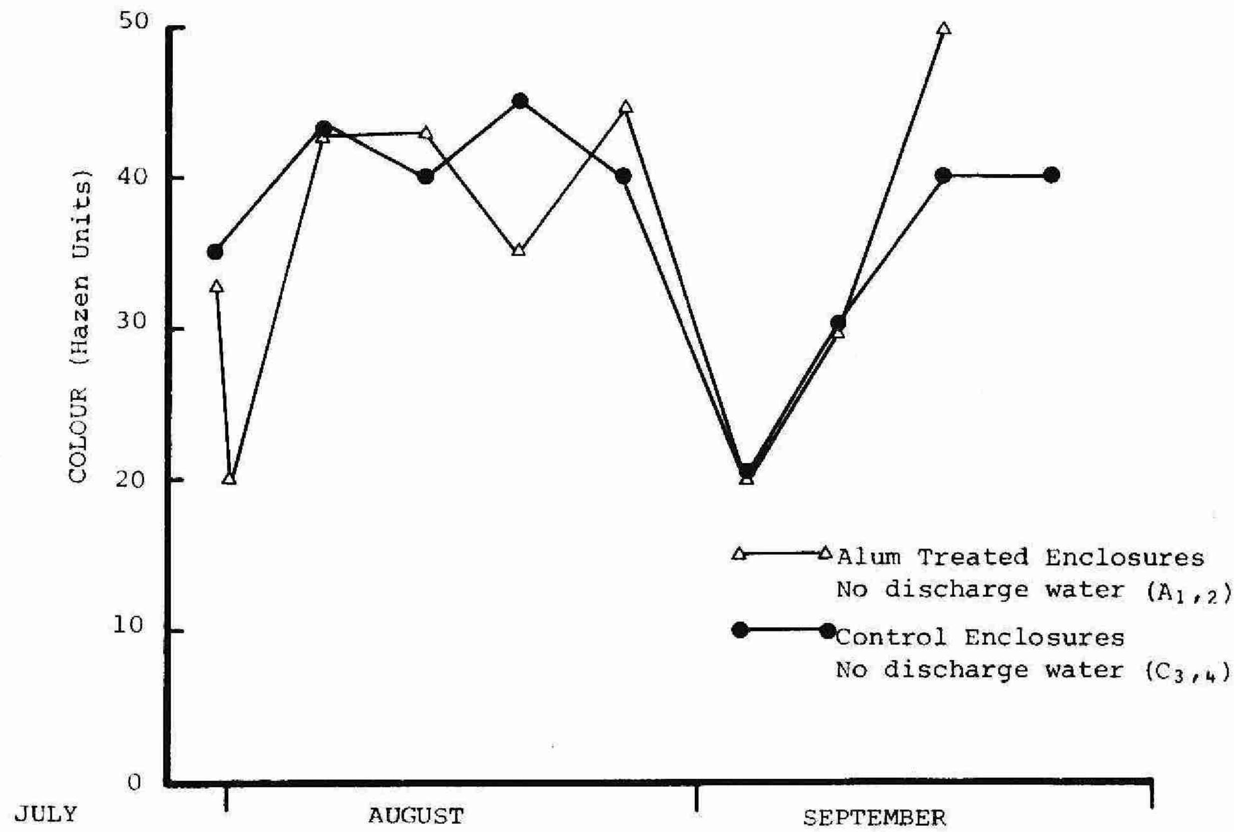
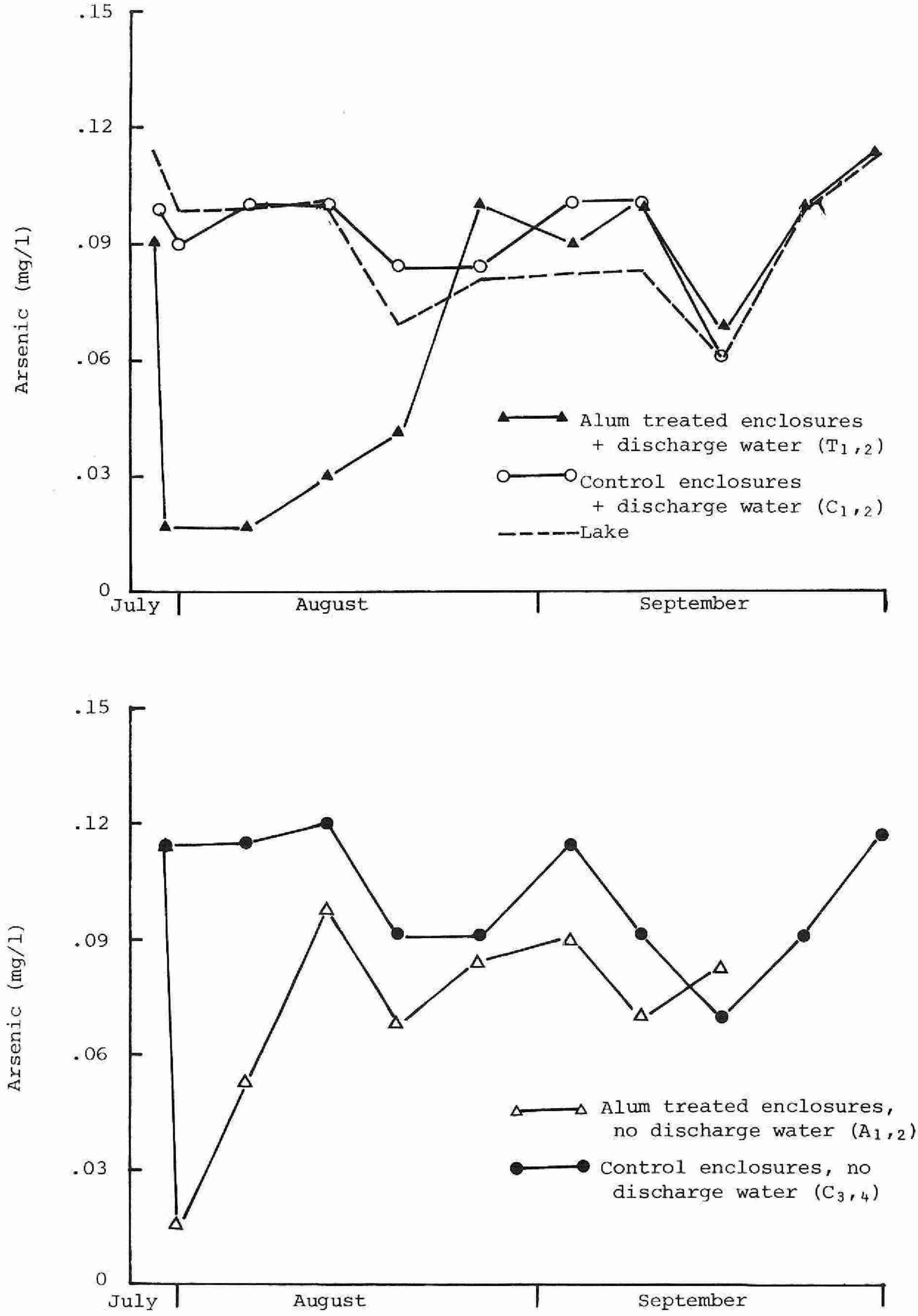


FIGURE 27: ARSENIC VARIATIONS IN TEST AND CONTROL ENCLOSURES AND LAKE WATER



Aluminum

Both enclosures $T_{1,2}$ and $A_{1,2}$ experienced peaks in aluminum levels from a pretreatment level of less than 0.04 mg/l to post-treatment levels (24 hours after treatment) of 0.98 and 0.72 mg Al/l respectively. (Fig. 28). Freeman and Everhart (1971) in studying the toxicity of aluminum hydroxide complexes to Rainbow trout stated that under constant flow situations the safe concentration of either dissolved or suspended aluminum is well below 0.5 mg/l. It would be expected, therefore, based on aluminum levels seen in enclosures $T_{1,2}$ that if the entire lake was to be treated, resident fish species would probably experience some degree of sub-lethal stress. The fact that aluminum values decreased to control and lake values within 33 days indicated that sub-lethal effects would be rather short-lived. Toxicity of aluminum to resident fish species should be thoroughly investigated prior to consideration being given to treat a water body with alum.

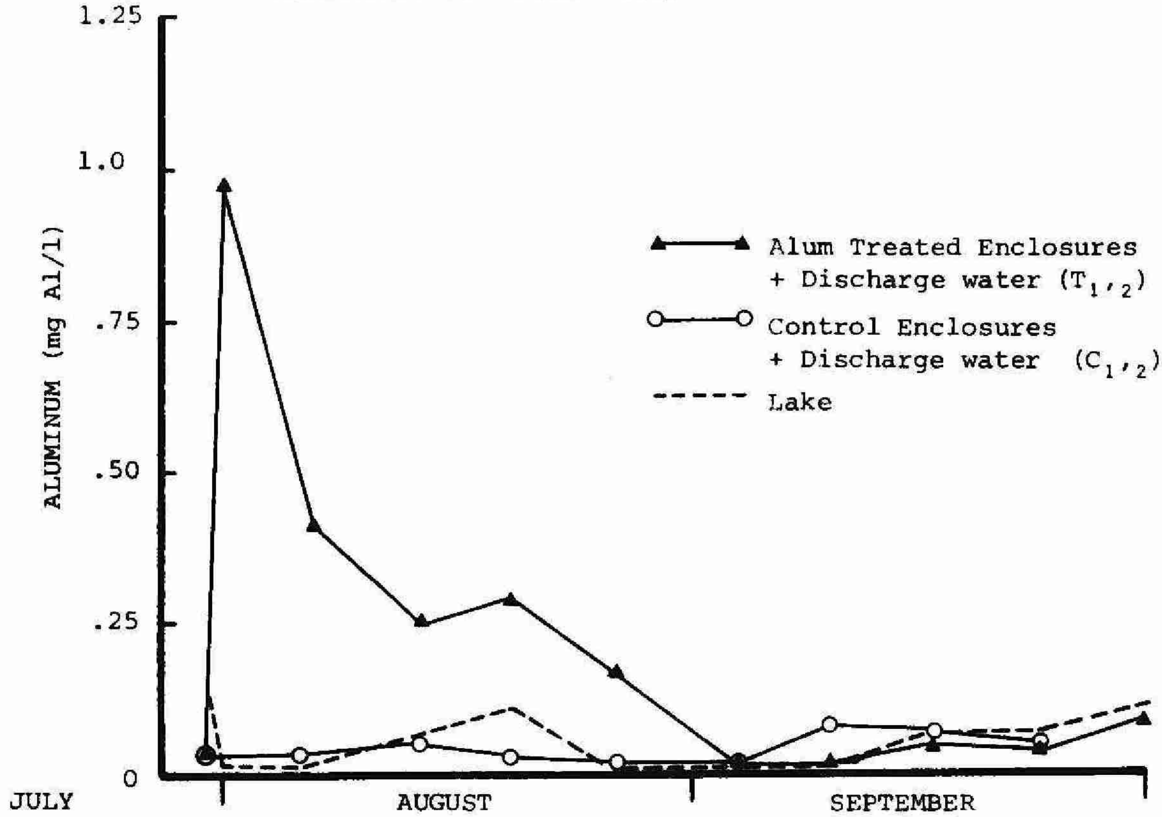
Sulphate

Following alum treatment there was a sharp increase in sulphate levels in enclosures $T_{1,2}$ and $A_{1,2}$ from a pretreatment level of 20 mg/l to a post-treatment level of 87 and 73 mg SO_4/l respectively. Figure 29 Based on hypothetical reactions the observed increases were in excess of 100% of the hypothetical values. Since total alum dosage was dependent on the volume of water to be treated it was evident that the calculations made were more than the actual volume of water present in the enclosures. Following the initial peaks, sulphate levels dropped gradually and returned to control levels by the first week in September. Although there was a significantly huge increase in sulphate content it is unlikely that these elevated levels would have any toxic effects on fish or invertebrates. Cairns and Scheier (1958) observed that the TL_m of sodium sulphate for the common bluegill (Lepomis macrochinus) was 13,000 mg/l for small fish (average 3.88 cm), 12,750 mg/l for the medium size fish (average 6.09 cm), and 12,500 mg/l for the large fish (average 14.24 cm). Freeman and Fowler (1953) observed that the 100 hr toxicity threshold for Daphnia magna to sodium sulphate was 3,642 mg/l.

Other Parameters

The aforementioned parameters demonstrated a definite affect as a result of alum treatment.

FIGURE 28. ALUMINUM VARIATIONS IN TEST AND CONTROL ENCLOSURES AND LAKE WATER



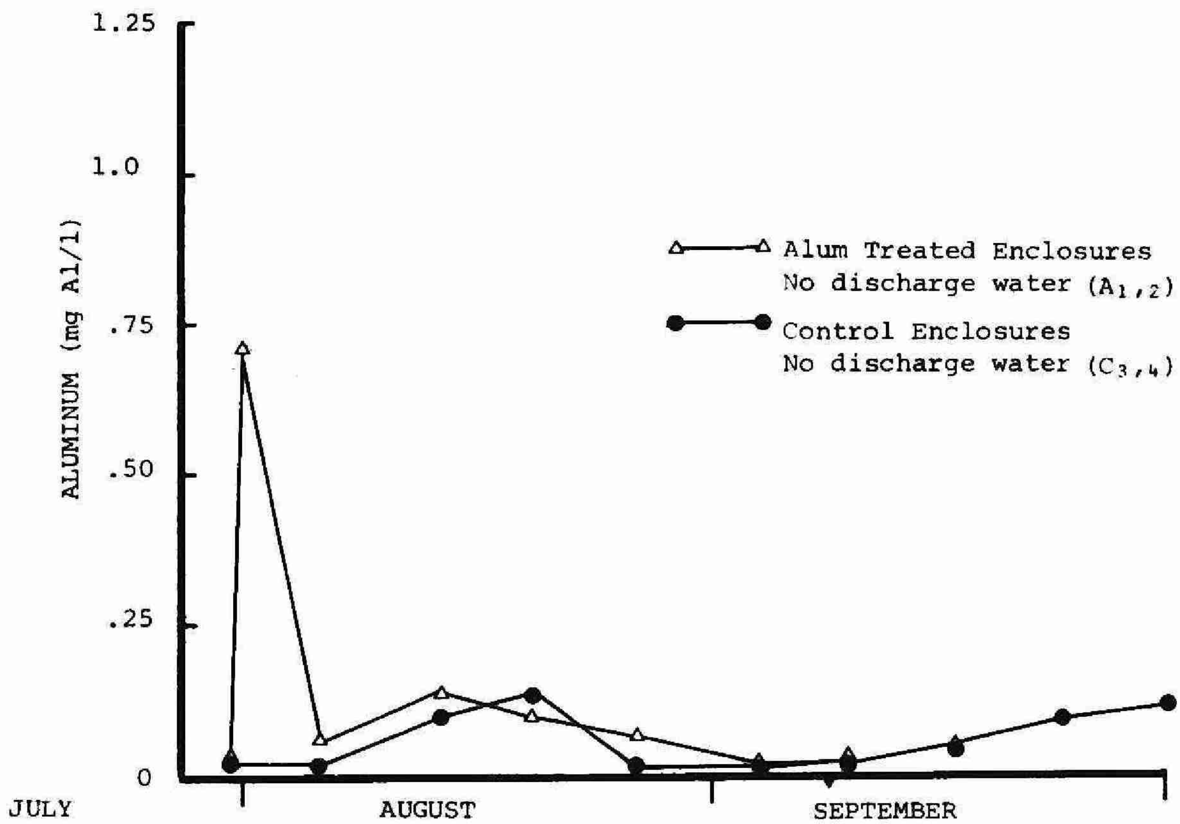
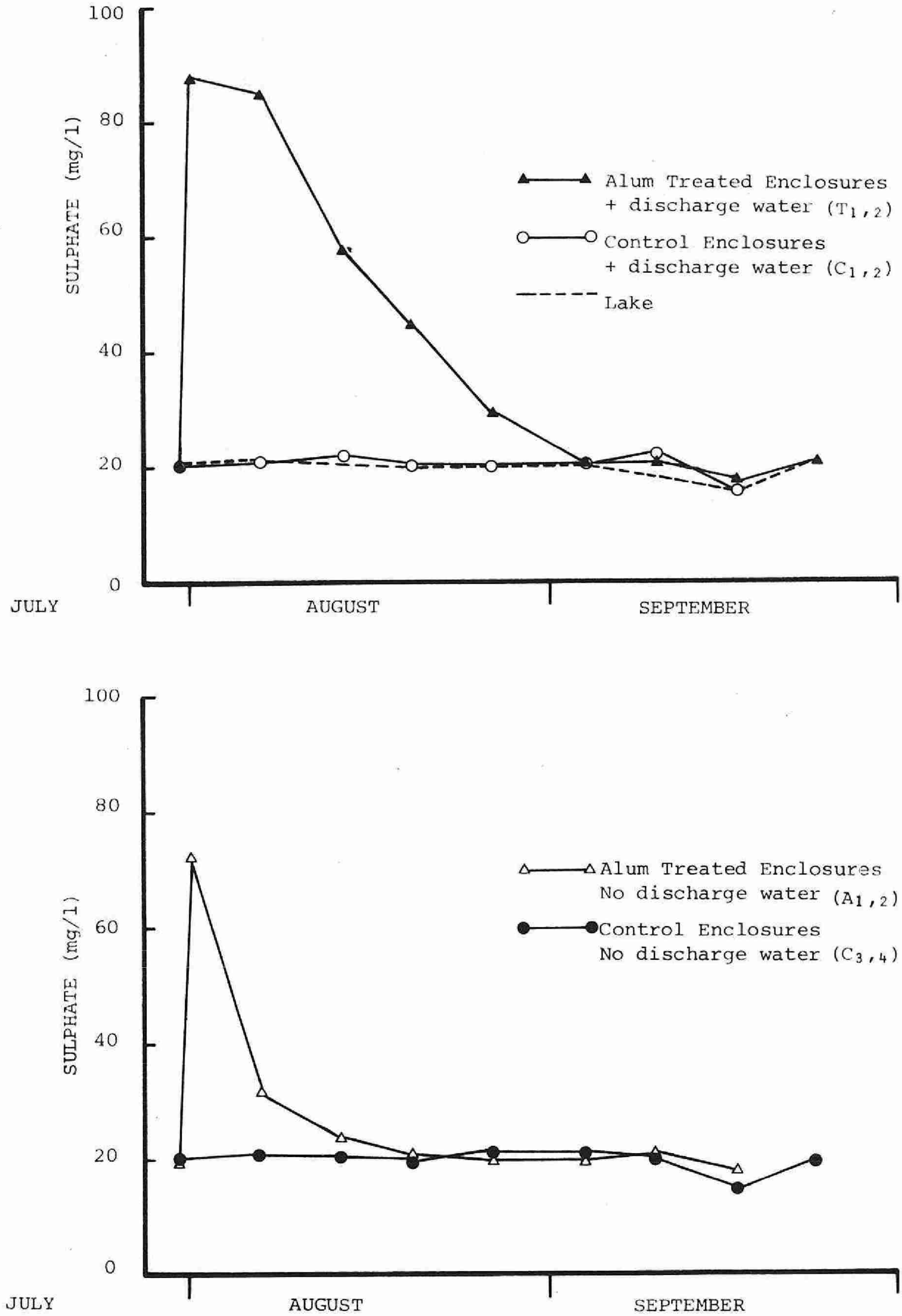


FIGURE 29. SULPHATE VARIATIONS IN TEST AND CONTROL ENCLOSURES AND LAKE WATER



Alum treatment demonstrated a reduction on both total and inorganic carbon that was rather short-lived in nature. Likewise BOD values were reduced in the test enclosure by approximately 67% (from 3.0 to 1.0 mg/l) but this reduction only lasted for 14 days. Conductivity values showed only a small increase.

Turbidity values in enclosures $T_{1,2}$ and $A_{1,2}$ were slightly higher than control enclosures for a short period of time following treatment.

No effect was seen on levels of manganese, calcium, silica, magnesium, potassium, sodium, iron or hardness.

CONCLUSIONS

In both the M.T.R.C.A. Pond Study and the Moira Lake Nutrient Inactivation Feasability Study significant improvements in water quality were seen in terms of nutrient and phytoplankton standing crop reductions accompanied by overall aesthetic improvements such as increased water transparency (M.T.R.C.A.) and colour reductions (Moira Lake).

The effective permanence of alum treatment was mediated by run-off effects and discharge water additions.

The use of *in situ* experimentation to assess the feasability of alum treatment lessened the predictive accuracy of the study due to containment affects exerted by the polyethylene enclosures.

Based on the results of both studies it became apparent that alum treatment is more efficient in an enclosed system than in a flow-through situation (Moira Lake). From a cost-benefit point of view a proposed alum treatment in the West Basin of Moira Lake is not feasible since the cost of chemicals alone ranges around $78,000 for a water quality improvement duration of approximately one month. On the other hand treatment of enclosed systems such as the M.T.R.C.A. Pond is feasible from a cost-benefit point of view.

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